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Physics. — *The structure of the Fluorine spectrum (F. I.).* By T. L. DE BRUIN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of December 18, 1926).

1. *Termtable. Classification of lines.*

In a former paper in these Proceedings [1]) I have deduced from the measurements of GALE and MONK [2]) and the observations of CARRAGAN [3]) of the ZEEMAN effects six multiplets in the *F. I.* spectrum, including most of the observed strong lines. Since a paper has been published by H. DINGLE [4]) concerning the *F. I.* spectrum, containing new and more precisely experimental data. DINGLE has produced the spectrum by a discharge in $Si\,F_4$. All our terms $(^4P, ^4P', ^4S, ^4D, ^2P, ^2P')$ have been found independently by DINGLE. The line $\nu = 13302{,}7$, calculated by me has been observed too. Far in the red DINGLE has observed a new line (2)7607,2 13141,8 [5]). A number of faint lines reported by GALE and MONK are not present in the discharge used by DINGLE. On the contrary a number of new lines, attributed to *Si* or *F* are present. DINGLE has extended the termscheme with a new term ^2P, $\triangle\nu = 532{,}7$. DINGLE notes this term as doubtful, because the ZEEMAN effect does not agree with the classification.

7	n^2P_2	250.3	n^2P_1
	4		(0—2)
b^2P_2	7800.6		(7956.0)
	12816.0		(12565.7)
325.8			
	2		5
b^2P_1	7607.2		7754.9
	13141.8		12891.5

---

[1]) T. L. DE BRUIN, Versl. Kon. Akad. v. Wet. Deel **35**, 751 (1926); (Proc. R. S. **30**, 20). See also Zeitschr. f. Phys. **39**. 10/11. 869. 1926.

[2]) GALE and MONK, Astr. Journ. **59**. 125. 1924.

[3]) H. CARRAGAN, Astr. Journ. **63**. 145. 1926.

[4]) H. DINGLE, Proc. R. S. London. Vol. **113**. A 764. 323. 1926.

[5]) This line is present in GALE and MONK's reproductions, but not included in their list.

The new line λ 7607,2 however forms with the unclassified line (5)7754,9 12891,5 the termdifference $\triangle\nu = 250{,}3$, present in our multiplet

TABLE 1 (Termtable).

Termsymbol	J	Termvalue (relative)	Termdifference	Combination with :
a^2P 1)	2	223296.9	325.2	^4P
	1	222971.7		
^4P	3	58617.0	274.7	$^4P'$, ^4D, n^2P, ^4S
	2	58342.3	160.0	
	1	58182.3		
$^4P'$	3	45104.8	122.9	^4P
	2	44981.9	102.7	
	1	44879.2		
^4D	4	44035.4	176.6	^4P
	3	43858.8	144.5	
	2	43714.3	83.4	
	1	43630.9		
n^2P	2	43400.0	250.3	^4P, b^2P
	1	43149.7		
^4S	2	42595.0		^4P
Z	2	42086.0		^4P
^2S	1	31959.0		m^2P
b^2P	2	30583.4	325.2	n^2P, m^2P
	1	30258.2		
m^2P	2	16377.8	145.0	b^2P
	1	16232.8		

---

1) This term is doubtful. It is possible that the observed ultra violet lines are due to the *ionized* atom.

4, of which it was not yet possible to give the termcombination. Now we can interpret multiplet 4 as a $^4P—n^2P$ combination and add a new multiplet $b^2P—n^2P$. There would be, in the region not yet investigated a line λ 7956,0.

All the terms, now obtained, are given in table 1. Because there is not a sure indication of series relation and the ionisation potential is unknown [1]), the term values are relative. The order is assumed from the term m^2P. [2])

TABLE 2. (Classification of F. I. lines).

Int.	λ	ν	Term-combination	Remarks
4	7800.6	12816.0	$n^2P_2 — b^2P_2$	[3])
5	7754.9	12891.5	$n^2P_1 — b^2P_1$	
2	7607.2	13141.8	$n^2P_2 — b^2P_1$	
2	7573.5	13200.3	$^4P_1 — ^4P'_2$	
2	7552.2	13237.5	$^4P_2 — ^4P'_3$	
0	7515.0	13303.0	$^4P_1 — ^4P'_1$	
1	7482.76	13360.4	$^4P_2 — ^4P'_2$	
3	7425.65	13463.1	$^4P_2 — ^4P'_1$	
6	7398.68	13512.2	$^4P_3 — ^4P'_3$	
5	7331.96	13635.2	$^4P_3 — ^4P'_2$	
2	7314.34	13668.0		
4	7311.13	13674.0		
3	7309.13	13677.8		
3	7202.44	13880.4	$b^2P_1 — m^2P_2$	
5	7127.989	14025.34	$b^2P_1 — m^2P_1$	
9	7037.560	14205.56	$b^2P_2 — m^2P_2$	
2	6966.430	14350.60	$b^2P_2 — m^2P_1$	
7	6909.884	14468.04	$^4P_1 — ^4D_2$	

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[1]) From the order of the deepest term a rough value of the ionisation potential will give ± 25 Volt. It should be remarked that this value would be anomalous in connexion with the deepest lying terms of *O* and *Ne* (O with 13.5 Volt *Ne* with 21,5 Volt). From a linear interpolation we can expect ± 17.5 Volt.

[2]) The order of the $^3_3$ terms should be $^1/_9$ of the Rydberg constant ± 12000.

[3]) Wavelengths without reference are due to DINGLE.

TABLE 2. (Classification of F. I. lines, *Continued*).

Int.	λ	ν	Term-combination	Remarks
9	6902.519	14483.48	${}^4P_2 - {}^4D_3$	
7	6870.287	14551.43	${}^4P_1 - {}^4D_1$	
10	6856.091	14581.56	${}^4P_3 - {}^4D_4$	
8	6834.327	14627.99	${}^4P_2 - {}^4D_2$	
2	6795.596	14711.36	${}^4P_2 - {}^4D_1$	
6	6774.039	14758.17	${}^4P_3 - {}^4D_3$	
4	6763.	14782.1	${}^4P_1 - n^2P_2$	G and M: 6762.91
1	6708.284	14902.84	${}^4P_3 - {}^4D_2$	
1$^1/_2$	6690.535	14942.37	${}^4P_2 - n^2P_2$	
0	6650.56	15032.2	${}^4P_1 - n^2P_1$	
4	6580.36	15192.5	${}^4P_2 - n^2P_1$	G and M
0	6569.785	15217.00	${}^4P_3 - n^2P_2$	
3	6416.30	15581.0	${}^2P_2 - {}^2S_1$	G and M
4	6413.695	15587.34	${}^4P_1 - {}^4S_2$	
1	6356.87	15726.7	${}^2P_1 - {}^2S_1$	G and M
5	6348.540	15747.31	${}^4P_2 - {}^4S_2$	
6	6239.693	16022.00	${}^4P_3 - {}^4S_2$	
3	6210.85	16096.4	${}^4P_1 - Z^2$	G and M
2	6149.77	16256.3	${}^4P_2 - Z^2$	G and M
4	6047.55	16531.0	${}^4P_3 - Z^2$	G and M
7	605.64	165114.6	${}^4P_1 - a^2P_1$	Millikan and Bowen 1)
	606.23	164955.5	${}^4P_2 - a^2P_2$	
	606.83	164790.8	${}^4P_1 - a^2P_1$	
	607.43	164628.0	${}^4P_2 - a^2P_1$	
	607.99	164476.4	${}^4P_3 - a^2P_1$	? (calc. 607.8)

Unclassified lines.

Three of the lines, common to the investigations of Gale, Monk, Carragan and Dingle (2)7314,34 (4)7311,13 (3)7309,13 are unclassified.

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1) These lines are observed by Millikan and Bowen: Phys. Rev. **23**, 1, 1924, Ph. Mag. **48**, 259, 1924.

The classification here given between brackets is doubtful.

DINGLE reports 12 faint lines (Intensity 0—1) due probably to *F* or *Si*. MILLIKAN and BOWEN have observed in the extreme ultra violet a group of 5 lines. We note the following regularity: ¹)

TABLE 3.

	λ DINGLE			λ MILLIKAN and BOWEN		$\Delta\nu$
1	6716.91	14883.7		656.00	152439.0	78.0
0	6751.94	14806.5		656.34	152360.1	116.1
1/2	6805.34	14690.3	5	657.84	152244.1	
				657.69	152047.3	143.2
				658.31	151904.1	

2. *The theoretical termscheme of F. I.*

HEISENBERG, PAULI and HUND ²) have developed a theory of complex spectra. In the light of this theory we shall deduce the theoretical term scheme of *F. I.*

The neutral fluorine atom has according to BOHR and STONER a group of 5 electrons in a 2_2 orbit. (Table 4). From considerations developed by PAULI and WENTZEL ³) such a configuration will give the same deepest lying term arising from the binding of one electron in a 2_2

TABLE 4*a*.

Z	*El*	1_1	2_1	2_2	Groundterm according HUND's theory	Groundterm exp.
4	*Be*	2	2	0	^1S	^1S
5	*B*	2	2	1	^2P	^2P
6	*C*	2	2	2	^3P	?
7	*N*	2	2	3	^4S	?
8	*O*	2	2	4	^3P	^3P
9	*F*	2	2	5	^2P	?
10	*Ne*	2	2	6	^1S	^1S

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¹) These groups could be combinations with another deep term than the ground doublet. In the theoretical termscheme (Table 5) deduced under 3 there is no place for such a term.

²) W. HEISENBERG, Zs. f. Phys. **32**. p. 841. 1925.
F. HUND, Zs. f. Phys. **33**. p. 345. 1925.

³) PAULI, Zs. f. Phys. **31**. p. 765. 1925.
G. WENTZEL, Zs. f. Phys. **31**. p. 445 1925.

orbit. For the ground term of Fluorine I we can expect a ^2P term as in B (Al, In, Tl). In the case of Fluorine this term will be "inverted" and the value should agree with the Röntgen L-doublet.

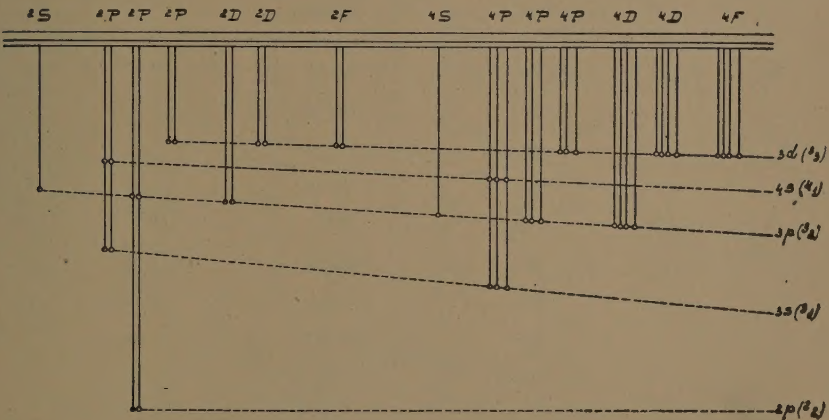
TABLE 4*b*.

	K	L_{11}	L_{21}	L_{22}	
9 F	2	2	2	3	$^2P_2$-Term
	2	2	1	4	$^2P_1$-Term

The other terms which would be expected, arise from the binding of an $3_1, 3_2, 3_3, 4_1 \ldots.$ electron to the ion (F^+). From the "Verzweigungsprinzip" of HEISENBERG and the experimental rule given by HUND:

$$|K_{\text{ion}} + K_{\text{elec.}}| - 1 \geqq l \geqq |K_{\text{ion}} - K_{\text{elec.}}| + 1$$

we deduce the following terms (Table 5). The figure [1]) illustrates the relative position of terms which could be expected. It is possible that the 3_3 terms are deeper than the 4_1 terms. Possibly there are also terms arising from the metastabil stages ^1S and ^1D of the ion. Such terms would not be expected to be presented by strong lines. Table 5 includes only the terms arising from ^3P.



Termscheme Fluorine (*F. I.*).

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[1]) The termscheme here deduced, holds also for the once ionised atoms of the rare gases *Ne II*, *A II*, etc. and the double ionized atoms of the alcalis *Na III*, *K III*, etc.

TABLE 5. Fluorine I (Deep terms).

Electron configuration							Basic term: ^3P	
							Terms	
nk 1_1	2	2_2	3_1	3_2	3_3	4_1	Quartet	Doublet
2	2	5						^2P
2	2	4	1				^4P	^2P
2	2	4		1			^4D ^4P ^4S	^2D ^2P ^2S
2	2	4			1		^4F ^4D ^4P	^2F ^2D ^2P
2	2	4				1	^4P	^2P

3. *Interpretation of the experimental terms.*

The agreement between the experimental and theoretical terms is not quite unsatisfactory. The terms ^2S and $^4P'$ are lying deeper than could be expected. We note that the ^2S term of *O II* 1) (this termscheme, as in the case *N I* 2) is based also on ^3P) exhibits this exception too and the exceptions of the intensity rule in the ^4P multiplets in *N I*, *O II* and *F I* have the same form. Table 6 gives an interpretation of the observed terms.

TABLE 6.

Exp.	Theor.
a^2P 3)	$^2P\,(2_2)$
^4P	$^4P\,(3_1)$
$^4P'$	$^4P\,(3_2)$
^4D	$^4D\,(3_2)$
n^2P	$^2P\,(3_1)$
^4S	$^4S\,(3_2)$
^2S	$^2S\,(3_2)$
b^2P	$^2P\,(3_2)$
m^2P	$^2P\,(4_1$ or $3_3)$

4. *Comparison with the spectra N I and O II.*

The basic term of these configurations is also a ^3P term (see table 4)

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1) A. Fowler, F. R. S. Proc. Roy. Soc. London. A. Vol. **110**. p. 476. 1926.
R. H. Fowler, F. R. S. and D. R. Hartree, Proc. Roy. Soc. London. A. Vol. **111**. p. 83. 1926.

2) C. C. Kies, Journ. Opt. Soc. America. Vol. **11**. p. 1. 1925.

3) Doubtful.

and by binding of an $3_1, 3_2, 3_3, 4_1 \ldots$ electron to the ion (N^+ and O^{++}), we obtain the same terms as in the case of FI (not from the addition of an 2_2 electron). Table 7 gives a comparison of the $\Delta\nu$ of analogous terms. The last part of the table shows that the interval proportion of the ^4P term, according to LANDÉ 5 : 3 (1,67) is in opposite sense in the case of the binding of an 3_2 and an 3_1 electron.

TABLE 7.

Basic term: ^3P		7	8	9		
Added electron	Term	*N.I*	*O.II*	*F.I*	$\frac{\Delta\nu . F_I}{\Delta\nu . N_I}$	$\frac{\Delta\nu . F_I}{\Delta\nu . O_{II}}$
3_1	^4P	47.07	158.52	274.69	5.37	1.64
		33.80	105.32	159.95		
3_2	$^4P'$	38.36	91.97	122.7	3.97	1.59
		18.38	46.10	102.7		
3_2	^4D	50.98	124.62	176.61	3.64	1.48
		37.35	91.56	144.51		
		22.59	55.54	83.38		
3_1	^2P	83.12	179.99	250.3	3.01	1.39
3_3	^2P	—	113.99	145.0	—	1.28
$\frac{^4P_{32}}{^4P_{12}}$:		1.39	1.55	1.72	Theor. LANDÉ 5 : 3 (1.67)	
$\frac{^4P_{32}'}{^4P_{12}'}$:		2.08	1.99	1.19		

Summary.

The analysis of the FI spectrum, has been briefly discussed in relation to the HEISENBERG-HUND theory. Between the experimental and the theoretical scheme is in general a satisfactory agreement.

December 1926. *Laboratory "Physica" Amsterdam.*

Physics. — *The melting-curve of helium and the heat-theorem of* NERNST. By W. H. KEESOM [1]). (Supplement N⁰. 61*b* to the Communications from the Physical Laboratory at Leiden).

(Communicated at the meeting of March 26, 1927).

§ 1. In the proceedings of the meeting of January 29, 1927 [2]) it appears that Dr. VAN LAAR objects to a passage in my Communication about the solidification of helium [3]), which passage concerns a relation between the course of the melting-curve and the heat-theorem of NERNST. This prompts me to give a more detailed explanation of the point in question. Further I will confine myself to two remarks on the case maintained by Dr. VAN LAAR.

§ 2. *What do the measurements concerning the melting-curve of helium teach about the heat-theorem of* NERNST?

I presuppose that we don't know anything about the course of the melting-curve of helium below 1° K. as long as we are in want of experimental data about that [4]). A course such as Dr. VAN LAAR gives, that is to say with a minimum at about 1° K., after that rising again at a diminishing temperature, to be tangent to the p-axis at 0° K., I don't think this to be impossible. But I don't think this course probable. Already the plain consideration of the part of the melting-curve known from the experiments (see Comm. N⁰. 184*b* Fig. 2) rouses as regards the continuation to the lower temperatures an expectation of going more and more parallel with the T-axis, rather than a bending in the sense of Dr. VAN LAAR.

In order to be able to criticize this more objectively two of my assistants have each noted down at my request the pressure of each 0.1 degree of a smooth curve (two curves drawn independently) of 1.2 to 3°.0 K., which as much as possible corresponds with the points of observation, have divided these pressures in two series of readings for values of T, which again and again differ 0.2 degree and have made up the second differences in these series.

Thus for each 0.1 degree was found an approximate value of $\frac{d^2p}{dT^2}$. The results are given in Fig. 1. Striking is the acute maximum at

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[1]) Abridged translation.

[2]) J. J. VAN LAAR, These Proceedings **30**, 244.

[3]) These Proceedings **29**, 1136. Comm. Leiden N⁰. 184*b*.

[4]) Except of course that it does not meet with the vapour-pressure-curve at the lowest temperature reached by KAMERLINGH ONNES and valued at 0.82° K.

1.8^{50} K. and the steep declining of the curve at lower temperatures. The latter is not in any part in keeping with that which Dr. VAN LAAR should wish.

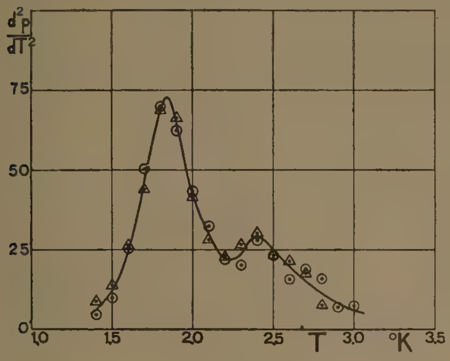

Fig. 1.

According to Dr. VAN LAAR at a sufficiently low temperature $\frac{d^2p}{dT^2}$ should be proportional to T^{-1} and so the curve for $\frac{d^2p}{dT^2}$, at diminishing temperature, should rise asymptotically to the p-axis. As the diminishing of $\frac{d^2p}{dT^2}$ between 1.8° and 1.4° K. will have to be considered as fixed by experiment, then according to Dr. VAN LAAR, the curve for $\frac{d^2p}{dT^2}$ should make a sharp bend upwards to the left. It is evident that experiment does not give any reason to think this probable in any way [1]).

For the sake of clearness — perhaps unnecessarily — I have put a formula of the form

$$p = aT \log T + \beta T + \gamma,$$

as Dr. VAN LAAR thinks probable (p. 248 l.c.) through the points 1,2°, 1,8° and 2,4° K. of one of the two drawn curves mentioned before corresponding as closely as possible to the observations.

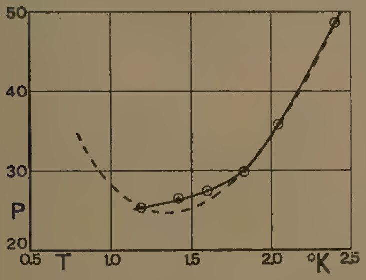

Fig. 2.

The result was: $p = 168{,}4\, T \log T - 95{,}32\, T + 123{,}72$. On Fig. 2 this curve (dotted line) has been drawn together with the experimental curve (drawn line). The deviations greatly exceed the experimental inaccuracy. Meanwhile it may be observed that it is perhaps not allowed to treat the coefficients a, β and γ as constants, that on the contrary they themselves must still be considered as temperature-functions. I should like to have this figure regarded only as an illustration of the fact, that the experimental curve has not at all the course of a curve, which goes through a minimum and after that will again strongly rise to the left, as Dr. VAN LAAR expects to be the case.

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[1]) I should not like to assert that the second top in the curve at 2,3° K. is real. It could be the consequence of the way of drawing the p, T curves. Meanwhile it is remarkable that both the assistants find this top and that it coincides with the place of the maximum of density of the liquid, see KAMERLINGH ONNES and BOKS, Leiden, Comm. N⁰. 170*b*, § 4.

Inferring from this, I think that as the most probable continuation of the experimental curve to temperatures below 1°.2 K, may be accepted a curve declining with a small bend. We may further accept that the curve will meet the *p*-axis at last with a horizontal tangent or that the curve still keeps a small inclination [1]).

If we now pass on the question, what follows from this in connection with the heat-theorem of NERNST, then we must keep the two possibilities just mentioned strictly apart. Perhaps it is a good thing to state here once more distinctly, that in both cases we bring about an extrapolation. Without extrapolation, however, nothing can be said about the theorem of NERNST. For the rest the region of temperature, over which the extrapolation extends itself here, is, expressed in degrees, many times smaller than with any other equilibrium examined in this sense, though with this we don't want to say that this last degree, which still separates us from absolute zero, might not still give extraordinary surprises. We must particularly leave open the possibility that between 1°.2 and 0° K. might still take place a transformation in the solid phase. However we here leave this possibility out of regard.

a. Let us then in the first place consider the case that $\frac{dp}{dT}$ for the melting-curve should approach to 0 at $T=0$. If we write the equation of CLAPEYRON in the form:

$$\frac{dp}{dT}=\frac{S_{liq}-S_{sol}}{v_{liq}-v_{sol}},$$

then follows that for $T=0$, S_{liq} should be $=S_{sol.}$ and so the entropies of the zero-point for the solid and liquid phase would be equal for helium. This then would be in strict correspondence with the heat-theorem of NERNST.

b. However if we accept that the melting-curve on approaching $T=0$ still keeps a small inclination and also, what seems probable, that $v_{liq}-v_{sol}$, though this difference is small (see Comm. N°. 184*b* § 3^b) keeps a finite value [2]), then from this should follow a finite difference for $S_{liq}-S_{sol}$ at $T=0$.

In order to get some opinion about the extent of such a possible difference of entropy we will put as final value at $T=0$ of $\frac{dp}{dT}$: 5 atm./°K.

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[1]) This last possibility has not been mentioned in Comm. N°. 184*b*. Also Dr. VAN LAAR does not speak about it. I especially wish to establish the fact here that this possibility must indeed not be lost sight of.

[2]) Should $v_{liq}-v_{sol}$ become $=0$ at $T=0$, then also in this case S_{liq} should become $=S_{sol}$ at $T=0$.

almost agreeing with the inclination of the melting-curve between 1°.2 and 1°.5 K. As to $v_{liq}-v_{sol}$ it follows from the visual observations mentioned in Comm. N°. 184*b* § 3^b, that this difference will only be a small fraction of for instance v_{liq}. If we put as utmost limit ¹) 5 % then we get $v_{liq}-v_{sol}=0{,}05\times7\times4=1{,}4$ cm³/mol. Then we should find $S_{liq}-S_{sol}=7$ atm. cM³/° K. mol. $=0{,}18$ cal./° K. mol. $=0{,}1\ R$.

This result, which is got with a value of $v_{liq}-v_{sol}$ which is very much greater than I think probable, is already one order of magnitude smaller than the differences of the zero point-entropies, which we find mentioned in literature as found or as probable ²).

The equation given by TAMMANN ³): $T-1=\log(p-24)$, which he emphatically wished to have considered as interpolation-formula and only applicable to a small region of temperature, would give a very much smaller value of $\frac{dp}{dT}$ for $T=0$, and so together with the value accepted for $v_{liq}-v_{sol}$ mentioned above a very much smaller value of the difference of the zero point-entropies, to say for the latter 0,004 R.

Even if the heat-theorem of NERNST in its former formulization according to which the entropy of a material at $T=0$ had to be the same in all conditions, provided they are condensed, should not be strictly valuable, then this would yet be very near the case for helium solid and liquid.

As a matter of course however the question arises here whether it is not to be considered probable on statistical-theoretical grounds that we must understand this result in this way that the entropy-difference between solid and liquid helium at $T=0$ becomes strict 0 instead of approaching to a small fraction of R.

Though in my opinion an answer to this question cannot be given with surety at this moment ⁴) yet I think that this fact that a value of $S_{liq}-S_{sol}$ smaller (probably very much smaller) than 0,1 R does not answer to the expectation that in $S'-S''=k\ln(z'/z'')^n$, the ratio z'/z'' of the probabilities of condition at $T=0$ can be expressed by a quotient of small whole numbers, gives cause to answer this question in the affirmative for the present.

§ 3. I might subjoin here still the following remarks ⁵).

1. I cannot perceive that Prof. PLANCK is guilty of a „thermodyna-

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¹) The small difference in refraction-index, which has to be accepted in order to explain that the surface of demarcation between solid and liquid was invisible, points to a very much smaller difference in density than was accepted here as highest limit.

²) F. SIMON, Handbuch d. Physik. X, p. 395, 1926. A. EUCKEN und F. FRIED, Zs. f. Phys. **29**, 36, 1924. A. EUCKEN, MÜLLER—POUILLET's Lehrbuch der Physik, 11te Aufl. Bd. III, 1ste Hälfte, p. 649. W. SCHOTTKY, Physik. Zs. **22**, 1, 1921; **23**, 9, 448, 1922.

³) G. TAMMANN, Ann. d. Phys. (4) **82**, 240, 1927.

⁴) See f.i. F. SIMON l.c., and Zs. f. Phys. **41**, 806, 1927.

⁵) In this translation the remarks have not been inserted to which Dr. VAN LAAR does not resert in his answer, These Proceedings, p. 957.

mical sofism" as Dr. VAN LAAR says. From the theorem which Prof. PLANCK puts first: „Beim Nullpunkt der absoluten Temperatur besitzt die Entropie eines jeden chemisch homogenen festen oder flüssigen Körpers den Wert Null" follows necessarily $\left(\frac{\partial v}{\partial T}\right)_p = 0$ at $T = 0$.

Whether this is deduced from that by the more detailed reasoning of Prof. PLANCK or by saying: $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ and so it follows from $\left(\frac{\partial s}{\partial p}\right)_T = 0$ for $T = 0$, that it must then be $\left(\frac{\partial v}{\partial T}\right)_p = 0$, is of no consequence.

The reproach that this theorem to be proved is already implied in the theorem from which is started, is not fair: it cannot be wished that from the premises something is being deduced that is not implied.

2. Dr. VAN LAAR cannot know that the specific heat of liquid helium by[1]) constant volume remains finite at $T = 0$ (loc. cit. p. 247). The experiments of DANA and KAMERLINGH ONNES[2]) which, however, don't go any further than 2°.5 K., would sooner give rise to expect that that specific heat does come up to 0.

Whether by liquids (and eventually by gases) at a sufficiently low temperature there appears a "degradation of energy" remains as yet an open question.

Wishing to derive from a presupposed opinion thereabout founded upon a very weak argumentation, that the energy in the liquid phase follows the T-law (VAN LAAR l.c. 247) is, to my opinion, not permitted.

If we follow the argumentation of Dr. VAN LAAR on p. 248 then it appears that the condition submitted by him that the $\frac{dp}{dT}$ for the melting-curve should become ∞ for $T = 0$ is only founded on this acknowledgement of the energy in the liquid phase.

While it appeared in § 2 that the direct experiments do not at all point to a course of the melting-curve at lower temperatures as is desired by Dr. VAN LAAR, we see here that this desire of Dr. VAN LAAR has no reasonable ground.

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[1]) It has not become clear to me what signifies here the addition "(infinitely great)".

[2]) L. I. DANA and H. KAMERLINGH ONNES, These Proceedings, **29**, 1061, 1926. Comm. Leiden N⁰. 179*d*.

Physics. — *The Melting-Point Line of Helium and* NERNST's *Theorem of Heat.* By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of October 29, 1927).

In connection with the considerations, published under the same title by Prof. KEESOM in these Proceedings, Vol. **30**, p. 952, I wish to make only one more remark.

Of course I admit that the course of the melting-point line from 4°,2 to 1°,2 K., as it has been derived by KEESOM from his measurements, leaves room for the supposition that $\frac{dp}{dt}$ steadily decreases on further cooling, and that $Lim. \frac{dp}{dt} = 0$ would be in agreement with NERNST's theorem of heat.

In my preceding communication (These Proc. Vol. **30**, p. 244) it was my intention to set forth that also another course of the melting-point line is not excluded at very low temperatures. I thought that I had reasons to expect such another course, and these reasons have not been affected by the further considerations and calculations to which Mr. KEESOM now subjects his measurements.

Indeed, Prof. KEESOM himself observes, that on approach of the absolute zero the last degree might bring surprises.

But there would not be any sense in continuing a discussion on this subject. We agree that only further experiments will be able to give certainty about the course of the melting-point line, still nearer to the zero point, and about the confirmation or non-confirmation of the conclusions which have been derived from NERNST's theorem of heat.

I hope to come back to the question concerning the specific heat of liquid Helium, advanced by Mr. KEESOM on p. 956 of these Proceedings, in a later communication; and as regards his remarks on my earlier criticism on PLANCK's *argumentation* (referring to the approach to zero of $\frac{dp}{dt}$ at $T=0$), I feel justified in fully maintaining what I wrote at the time.

Tavel sur Clarens (Suisse), October 1927.

Psychology. — *A statistic inquiry into the Psychic Differences between the Generations of To-day and Former times.* By D. WIERSMA. (Communicated by Prof. E. D. WIERSMA.)

(Communicated at the meeting of Sepember 24, 1927).

When people talk about the spirit of the age and ascribe to it all sorts of present-day views in the domain of science, art, and social life, or striking phenomena, they mean that in some respects the living generation differs from those of former times. Their thoughts, their sentiment and actions are not perfectly alike. Of course, in some respects this difference results from improvements in technics and in general insight: the achievements of former generations have placed at our disposal more and different data, that will cause our judgments, our actions, and in part also our emotional reactions to be different from those of former generations, had they been living under similar circumstances to ours. The fact that travelling has become more common than 30 or 40 years back, is no doubt owing to the great improvement in means of communication. That the latest suneclipse caused no terror and fear, as it did a few hundred years ago, but everywhere a lively interest of a more or less scientific character, is to be ascribed to a better insight into the nature of the phenomenon, which has now become quite familiar to us. Now, suchlike differences with former generations are not generally attributed to the spirit of the times. This term is reserved for the difference in psychic qualities of men of to-day and of former times. It seems interesting to me to ascertain to what extent these differences really exist and whether they can account for some specific peculiar features of our time.

Increased love of pleasure is often considered to be such a peculiar feature. The rage for dancing, the intense interest in cinemas, music-halls and coffeehouses go to prove this. But in earlier times almost every older generation judged of the younger one in the same way; this already must give us pause. The decreased use of alcohol, evident from the returns of the excises, from the frequency of drunkenness, and from the decrease of alcohol-psychoses, very manifest in the psychiatric clinic at Groningen, rather points to a new object of pleasure-seeking than to a greater love of pleasure.

A number of other features of our time may perhaps be classed as the results of a diminished sense for reality. The progress of anthroposophy, of theosophy, spiritism and the like shows that, rather than allowing themselves to be acted upon by nature and the human world about them, merely for judgment, sentiment and action, people of our time (more than former generations) place a higher value on ideas and emotions of their own, when forming an opinion of the world. That this opinion satisfies their own emotional desires seems to be of greater importance than adhering to observed facts; the interest of men has been transferred from the outer world to man's inner life with all its contrarieties and inconsistencies, which often reveal themselves in the most grotesque and worst founded constructions, often manifested again in the widely divergent philosophical speculations of our days.

There is no mistake, that also in Art a corresponding shifting of interest exists. The days of realism and naturalism have long gone by; art no longer interprets the world seen again "à travers d'un tempérament", but is rather devoted to the gratification of emotional wants. Impressionism still reproduced the reaction of the artist upon the outer world, expressionism is more removed from it, as the outer world becomes only a means to express the inner life of the artist. In various directions we can observe endeavours to get completely detached from the outer world. In literature as well as in the art of Painting, Sculpture and Music this tendency reveals itself, perhaps dadaism is one of its extreme excesses. Spiritualization and self-centralization are modern words expressive of a greater interest for inward than for outward experiences: to this tendency we owe besides works of grandeur also many strange, and grotesque creations. A certain disintegration is especially noticeable in a great number of various sorts of schools, but often also in the work of the same artist.

Science also presents a tendency to turn aside from reality. More often than formerly Reasoners start from pre-conceived ideas, fitting in with their conception of the world, while their respect for real facts has diminished. Another result of it is the co-existence of very many views of which the representatives are reasoning away without being understood, as well as a certain vagueness and want of exactitude. Quite recently these phenomena have been signalled by HOCHE (4), who also ascribed them to a lessened sense for reality. Experimental psychology e.g. which works purely inductively, does not go through a golden period now, whereas phenomenology does, as it bears on the subjective experiences of man. Just as in Art, a tendency to disintegration may be observed: whereas in days of yore researchers tried to find only the causal connection of phenomena, those of the latter years have emphasized the so-called conceivable relations which are supposed not to have anything to do with causality. This new orientation, which has also been introduced into physiology and other branches of science, has no doubt furnished important results; I only mention the fact to point to the change without entering into an appreciation of the several directions.

We said that nowadays a general tendency may be observed to avert from the outer world, and to be wrapped up in one's own thoughts and inner life, which BLEULER (1) has styled "autistic" thinking, thereby to point to the resemblance such a mode of thinking bears with that of a man in a certain psychosis: "dementia praecox". JASPERS (5) in his monograph *Strindberg und Van Gogh* calls attention to the present predilection for the schizophrene phenomena and even non-psychologists

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were struck by this resemblance. I remember a caricature in the weekly paper "Life", which ridiculed all sorts of peculiarities of modern life, with the subscription: "our time suffers from dementia praecox".

It has often been presumed that these peculiarities of the present generation are to be considered as a consequence of the war; but it should, on the contrary, be remarked that the modern peculiarities regarding view of life, and conceptions of art and science had already extisted for a longer or shorter time before the war, only they became more pronounced and striking after it. It will therefore be our task to ascertain whether in the present generation a greater frequency can be found than in older generations, of properties that can account for the peculiarities discussed above.

Splendid material for this investigation is supplied by the research-work done by HEYMANS and WIERSMA in 1905 and 1923. The first inquiry (2), as known, was intended to establish the heredity of psychic properties; therefore in this inquiry a comparison was also made between the older and the younger generation and was described in detail by the authors (3). The second inquiry (8) was made to observe whether there was a relation between physical stature and psychical qualities; it will therefore be designated as stature-inquiry, although in this paper I shall busy myself only with the psychological part, which regarded the same properties as those of the heredity-inquiry. The results of the two inquiries present in general a striking resemblance, bespeaking their reliability. Still, differences do occur, no doubt. They are to be ascribed to the different views of the reporters. This plays of course a much greater rôle in the stature-inquiry, which comprised 400 subjects, than in the heredity-inquiry extending over 2500 persons. For the determinations of the magnitude of a difference, that may be attributed to mere chance only, I followed the same method applied by HEYMANS and WIERSMA for an intercomparison of groups falling within the heredity-inquiry, viz. a comparison of the procentic values for the properties, asked for in the first 8 questions. For men, as well as for women, the mean difference lay between 4 and 5, so that the assumption is admissible that an increase or a decrease of the percentage of some quality or other of 4 or 5 or more, rests on an other basis than mere chance.

So we are in a position to compare the older generation of the heredity-inquiry with the younger generation of the same inquiry and with the generation of 1923, which is expressed in the stature-inquiry. As to age the last two can easily be compared with each other. The age of the men of the younger generation of 1905 averaged 35, that of the men of 1923, 43; the women respectively 33 and 39 years. The older generation of 1905 was, of course, much older, the mean ages of men and women being here respectively 67 and 63, some differences found might, therefore, be based on normal differences in psychic qualities, shown by older people, as compared with younger ones. When we find, however, that the difference of certain properties shown by the younger generation of 1905, has become still greater, then we may assume that we have not to do with a difference in age, but a difference in properties of the generations themselves. For since the generation of 1923 is on an average older than that of 1905, a difference in age would have become less evident instead of more evident.

Now, first of all as regards an increased love of pleasure, the results do not tally completely with the current opinion. In our investigations we inquire after a fondness of good cheer, after the use of alcohol, extravagance in sexual life and a fondness of going out. The procentic values found have been tabulated below (*s* = the older *j* the younger generation).

TABLE I.

a. Men.

	1905 s.	1905 j.	1923
Fondness of good cheer	43	49	51
Not	37	30	21
Drunkard	3	1	1
Regularly	31	20	9
Occasionally	50	57	63
Never	13	11	16
Sexual extravagance	6	11	12
Reserved	69	58	65
Going out	24	32	20

b. Women.

	1905 s.	1905 j.	1923
Fondness of good cheer	30	31	30
Not	50	42	40
Drunkard	0	0	0
Regularly	3	2	1
Occasionally	47	45	45
Never	30	30	30
Sexal extravagance	2	2	6
Reserved	69	58	70
Going out	19	35	23

These tables show, indeed, a lessening in the use of alcohol for either sex. Men, on the contrary display an increasing inclination to good cheer; for women we obtained smaller percentages in this respect. The results regarding sexual propensities are peculiar. In the two sexes there is a higher degree of extravagance, especially among the women of the youngest generation. On the other hand, also the percentages of reservedness have risen considerably in 1923. For the present I cannot say for sure, what is the cause of this result; anyhow it is clear, that it would not be right to speak of a general tendency to sexual indulgence. As to pleasure-seeking, in 1905 the younger generation seemed to be much fonder of going out than the older one, but in 1923 this augmentation is not noticeable. This is perhaps due to the fact that in 1923 frequenting coffeehouses and cinemas had become so common, that the reporters have taken notice only of the extreme cases. In that case the percentages of 1905 and 1923 are not comparable. Some figures representing behaviour in money-matters are at our disposal, an augmentation of sensual pursuits will readily involve greater wastefulness, a regress of economy. Table II gives the percentages.

TABLE II.

a. Men.

	1905 s.	1905 j.	1923
Avaricious	2	3	1
Economical	44	35	53
Free-handed	41	41	39
Lavish	2	10	2
In debt	3	6	5

b. Women.

	1905 s.	1905 j.	1923
Avaricious	3	2	1
Economical	56	46	49
Free-handed	29	34	41
Lavish	2	6	3
In debt	2	1	2

These figures show a marked resemblance to those concerning pleasure-seeking and going out; the younger generation of 1905 shows a marked diminution of economy and an augmentation in liberality and lavishness, which has been compensated for in 1923. The first researchers (3) suspected that the difference found between the two generations of the heredity-inquiry has to be attributed chiefly to the difference in age and not to a real change in the qualities of character. This seems to be well confirmed by our results. Of course, it is only just to point to the possibility, that the data of the stature-inquiry, so much more limited than the heredity-inquiry have been derived especially from the better-bred class of people, who are less fond of amusement and are more inclined to economy, and that these data are, therefore, less fit for comparison with those of the heredity-inquire, the increase of the love of pleasure as a typical feature of modern we are not justified in considering, on the basis of the results of this inquiry, the increase of the love of pleasure as a typical feature of modern times. There are facts pointing in this direction, but also others that point the other way.

In the second place we have to ascertain whether the phenomena, grouped together as the consequences of a decreased sense for reality, are again met with in the data of our inquiries. As has been stated before, these phenomena remind us of those of dementia praecox, in so far as they bear some resemblance to one of the most important symptoms of this disease, viz autism. Now, some years ago a comparison of the data of the heredity-inquiry with anamnesis of the characters of a number of people, who afterwards had contracted dementia praecox, enabled me to point out a correlation of the properties of a group of men, marked by a taciturn and solitary character, with the future sufferers from dementia praecox (6). We could recognize a number of properties, known to us, when exaggerated to a pathological degree, as symptoms of dementia praecox, in a smaller degree in the two groups examined, but more frequently than is expressed in the general percentage of the heredity-inquiry. Afterwards I was in a position to demonstrate (7) that the maniac-depressive psychosis, when occurring in taciturn, solitary men, can reveal under the influence of this type of character, remarkable peculiarities of the clinical aspect and course which remind us of dementia praecox. Now, since many characteristics of the modern mental attitude remind one of this psychosis, I think it interesting to inquire whether taciturnity and solitariness, and some qualities that show a correlation with the above-named character-types, are perhaps demonstrable among the younger generations in increasing frequency. Such qualities are timidity in company, closeness, losing oneself in abstractions, and absent-mindedness. The taciturn and solitary people often do not feel at ease in society, they do not present themselves such as they are, but are somewhat constrained in manners, which is an indication of the mannerism of many praecox-patients. Their sympathies and their antipathies, their intentions and their emotions they often keep back ; this is their closeness, which we may observe in much larger measure in cases of dementia praecox. Often the taciturn and solitary get absorbed in abstract meditations, mostly of a philosophical or a religious nature, they are apt to take a biassed view of the world, which corresponds

TABLE III.

a. Men.

	1905 s.	1905 j.	1923
Conversational	64	64	59
Loquacious	12	8	9
Taciturn	15	19	19
Interested in recreation	24	32	20
Fond of home-life	65	49	61
Solitary	6	11	14
Constrained	15	21	20
Close	35	34	43
Abstractions	15	19	34
Absent-minded	18	27	29

b. Women.

	1905 s.	1905 j.	1923
Conversational	71	70	67
Loquacious	5	6	4
Taciturn	15	15	19
Interested in recreation	19	35	23
Fond of home-life	69	52	70
Solitary	6	5	6
Constrained	17	18	13
Close	35	30	35
Abstractions	10	11	15
Absent-minded	20	19	25

with the grotesque fancies of numberless praecox patients. In fine the taciturn and solitary display a high degree of absent-mindedness, they take little notice of what happens in the world round about them, as they are absorbed in their own thoughts. The same is observed in a larger measure in dementia praecox. The procentic values for the various generations of normal men I subjoin in Table III.

It will be seen from these figures that there is a remarkable difference between men and women. The men not only show a marked increase of the two chief qualities of the type in question, taciturnity and solitariness, but also of all qualities mentioned and correlated with these two. Apparently they live less in the outer world, lose themselves more in their own thoughts and emotions than earlier generations. They are less communicative, they have become more taciturn, and more close: they keep back their intentions and emotions. Instead of taking an interest in passing events, they live in a sphere of their own, which is apparent from the more pronounced solitariness, and an increased inclination to abstract meditation. More than formerly they are absent-minded, i.e. they adapt themselves less completely to the stimuli received from the outer world ; they do not feel so well at home in that outer world as people did formerly, which appears from their constrained attitude, they have lost their bearings. The same predilection for their own thoughts and emotions we could observe in the modern views of the world and the interpretations of Art and Science nowadays. Especially the tendency to abstractions is unmistakable here. As is also borne out by our figures, it is also largely increased.

Now there are also some qualities, correlated with the taciturn and solitary type, which are not increased in frequency in the most recent generation. To this class belong : suspicion, lack of wit and humour, selfishness and a deficient perceptive faculty. But at least of the first of these qualities it may be assumed, that they are also distinctly correlated with other qualities of temperament and character, while they can serve no more as types of the syndrome of dementia praecox, than as types of the spirit of our age. Something like this also applies perhaps to a weaker power of observation, but a closer inspection will have to make this out.

The figures of the women present another picture. The women have become a little less communicative [1]), but not more solitary. Apparently they do not feel less at ease in the world than formerly, anyhow they exhibit rather a diminished than an increased constraint in their behaviour, neither have they become closer than before. Although less intensely than among men their bias towards abstract meditations has increased, just as their absent-mindedness. So a slight shifting of the character-type in the same direction as with man can also be observed, but for women it is far less pronounced. But since in science as in art, and also as regards views of life, men generally take the lead, it cannot be surprising that this shifting of the character-type of men has expressed itself indubitably in what is commonly called the spirit of the times. I have stated already that this change does not result from the war. This appears, moreover, distinctly from the results of the inquiries which show, that the changes discussed, had begun to reveal themselves already in 1905 in the younger generation.

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[1]) Just as with men the rise of the percentage for taciturnity lies on the very border of what may probably be called fortuitous. As however the percentage for good conversation has fallen conformably, we feel justified in assuming in this case a fortuitous change of the number.

Although it is perhaps unnecessary, I will emphasize the fact, that this psychic change in modern man is not at all pathologic. That there exists a conformity of the taciturn and solitary character to dementia praecox patients, does not imply that the former have dementia praecox to a slight degree. The nature of the correlation of character with disease has not been fully established. It is uncertain whether dementia praecox should be considered simply as a pathological exaggeration of the taciturn and solitary character-type. Still, even if this should prove to be the case, an increase of the character-type among people in general is of no greater significance than any change of character or temperament would signify, as we know that every type of character or temperament leads in its extreme excesses to psychic anomalies.

That in our days woman accommodates herself to altered conditions in the world better than in former times, which assertion is substantiated by less constraint in her behaviour, is not surprising, as woman's position in the world has been greatly altered during the latter decennia. Ways are opened for her in every sphere of labour, in every branch of study ; like man she can choose her pursuits after her own liking. Her dependence on, and inferiority to man, has entirely disappeared, and qualities, formerly considered as female virtues, such as abstaining from forming an opinion of her own, a tendency to keep in the background, and to follow the lead of man, are now looked upon as a sign of inferiority, just as they are for men. Woman could not but adapt herself to these altered social conditions, and become more independent. This is, indeed, borne out in the subjoined table (Table IV).

From this table it appears that the tendencies to repeat another's words, to keep in the background, to follow the lead of others and be overruled, formerly oftener met with among women than among men, now occur more frequently among the latter. Conversely, in our time women surpass men in regard to domination. These changes also are not of recent times, but were already distinguished in 1905. Moreover, the whole table shows, that the values for the two sexes are drawing together, which began already in 1905 with the younger generation, and is also clearly visible in 1923, although not more pronounced. In regard to these qualities, which clearly show the degree of independence, this levelling is in strictness nothing particular. It can hardly be doubted that there is a causal relation here with

TABLE IV.

	1905 s.		1905 j.		1923	
	M.	W.	M.	W.	M.	W.
Resolute	51	49	50	53	57	53
Irresolute	29	29	30	28	23	19
Independent	69	56	64	59	71	67
Parroting	13	24	20	24	13	10
Ambitious	38	25	34	30	26	20
Indifferent	24	16	26	24	19	17
In the background	19	32	16	20	28	26
Domineering	24	23	19	25	15	21
Giving full scope	55	43	53	47	67	53
Amenable	12	17	13	13	5	4
Going in for polities	12	1	7	2	6	3

the feminist-movement, though we are not quite sure where to look for the cause, and where for the effect. Is the greater independence of woman a consequence of the feminist-movement, or is the latter the result of woman's greater independence? In the first case we cannot assume a real change in men, no more than in the case of the past fear of suneclipses: people have merely adapted themselves to altered circumstances. In the second case, however, a real psychical change in woman is perhaps answerable for the feminist-movement. In order to ascertain this a closer inspection of other qualities is required. For some intellectual qualities we get the following values: (See Table V, p. 968).

From this we see that the large difference in favour of man in the younger generation of 1905 seemed to have disappeared almost completely, but that in 1923 it re-appears, although reduced to little more than one third, as compared with the older generation of 1905. Now a marked tendency to levelling of the differences between man and woman had been established by HEYMANS and WIERSMA (3) for the younger generation of 1905, especially for the secondary function, of the intellect and of most inclinations. All these groups of qualities yield the same results in 1923 as those just mentioned; the sex differences are, indeed, much smaller than for the oldest generations of 1905, but again considerably larger than for

TABLE V.

	1905 s.		1905 j.		1923	
	M.	W.	M.	W.	M.	W.
Quick of apprehension	60	49	59	57	70	66
Intelligent	60	45	51	44	60	50
Shallow-minded	13	23	18	19	6	10
Stupid	2	5	4	5	0	0
Memory:						
Extraordinary	17	11	12	8	13	14
Good	75	74	75	78	68	67
Bad	4	9	7	7	8	10

the youngest of that year. This levelling also continued in 1923 only for the qualities that point to a higher degree of independence and activity in social life. I feel inclined to conclude from this that the increase of the latter qualities is partly ascribable to the altered circumstances, anyhow for women. Better education, a wider scope of activity have given the girls more independence of judgment and attitude. Besides, also a general tendency is observable to a lessening of the differences between man and woman, which became more apparent in 1905 than in 1923 and of which the secondary character has not been identified. In connection with the new fashions in clothing and head-dress, in sport and in life-maxims we often hear people speak of the growing "masculinity" of woman. Except with respect to independence, this tendency, which cannot be other than a greater psychical likeness of the two sexes, is not increasing. Probably, however, most of these mannish phenomena among the woman-fashions of to-day may be considered as signs of an increased independence. The press contains repeated utterances suggesting that short frocks, bobbed hair, greater love of sport, are considered as such. This generally observed phenomenon is affirmed by our figures.

I am perfectly aware that much remains to be said about the spirit of our age. An inquiry into the relative frequency of the various qualities of temperament separately and collectively, into the increase or decrease of religiosity e.g., which has also been much debated, would no doubt yield interesting results. I believe, however, that in themselves the results discussed justified a publication. They may be summarized as follows:

1⁰. Increasing love of pleasure cannot be considered as a typical mark of our time.

2⁰. Many peculiarities of modern thought, which may be considered as a lessened sense for reality, are easily comprehensible through the greater frequency of the taciturn and solitary character-type, which is especially notable in man.

3^0. In psychic qualities the woman of our time differs, broadly speaking, less from man than formerly. This levelling is most pronounced and most constant in regard to qualities that point to greater independence, and is as such decidedly partly a consequence of the feminist-movement.

From the Psychiatric-Neurological Clinic
of Groningen.

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Physics. — *The fundamental pressure-coefficient of helium.* (Communication N^{0}. 188*a* from the Physical Laboratory at Leiden). By W. H. Keesom and Miss H. van der Horst.

(Communicated at the meeting of September 24, 1927).

§ 1. *Introduction.* The fundamental pressure-coefficient, i.e. the pressure-coefficient between the fundamental points 0° and 100° C., for helium had not been directly measured in Leiden. Cath and Kamerlingh Onnes 1) determined the difference of the fundamental pressure-coefficients for the international helium and hydrogen thermometers with the differential gas thermometer 2). They found $\alpha_{iH_2} - \alpha_{iHe} = 0.0000014$. With $\alpha_{iH_2} = 0.0036626$ 3) this gives $\alpha_{iHe} = 0.0036612$ 4).

This value only differs little from the value $\alpha_{iHe} = 0.0036614$, which was deduced from the pressure-coefficient assumed in Leiden for the Avogadro state $\alpha_A = 0.0036618$ by means of the values $B_{0^\circ\,C.}$ and $B_{100^\circ\,C.}$ determined by Kamerlingh Onnes 5) 6).

However it remained desirable to measure the pressure-coefficient for helium directly. This was all the more necessary as Henning and Heuse 7) deduced from direct measurements $\alpha_{iHe} = 0.0036600$.

These measurements by Henning and Heuse, however, are subject to serious objections. For instance their simultaneous measurements of pressure- and expansion-coefficient for helium lead to values of $B_{100^\circ\,C.}$, which are neither in mutual agreement nor in agreement with those of other experimenters 8).

We have now measured successively the pressure-coefficient of helium with two different gasthermometers.

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1) P. G. Cath and H. Kamerlingh Onnes. Arch. Néerl. (III)A 6, 1, 1922. Comm. Leiden N^{0}. 156*a*.

2) By international helium and hydrogen thermometer is meant the thermometer in question at constant volume with initial pressure $p_{0^\circ\,C.} = 1000$ mm. Cf. H. Kamerlingh Onnes, these Proc. **10**, Febr. 1908 p. 589, Comm. Leiden N^{0}. 102*b* and further W. H. Keesom and H. Kamerlingh Onnes, Suppl. N^{0}. 51*a*, § 2, 6 and § 9, 1.

3) According to H. Kamerlingh Onnes and M. Boudin, these Proc. **3**, Sept. 1900, p. 299, Comm. Leiden N^{0}. 60, where $\alpha_{vH_2}^{0^\circ-100^\circ\,C.} = 0.0036627$ was found for $p_{0^\circ\,C.} = 1098$ mm.

4) Cath and Kamerlingh Onnes put $\alpha_{iH_2} = 0.0036627$, cf. Comm. N^{0}. 156*a* p. 18 note 4. Cf. Suppl. N^{0}. 51*a*, p. 13, note 5.

5) H. Kamerlingh Onnes. These Proc. **10**, Dec. 1907, p. 445, Comm. Leiden N^{0}. 102*a*.

6) See Cath and Kamerlingh Onnes, Comm. Leiden N^{0}. 156*a*, p. 22, note 1.

7) F. Henning and W. Heuse, Zs. f. Phys. **5**, 285, 1921.

8) From the data on this subject given by Henning and Heuse above referred to we find by:

$$\alpha_v^{0^\circ-100^\circ\,C.} - \alpha_p^{0^\circ-100^\circ\,C.} = B_{100^\circ\,C.} \cdot \alpha_A \cdot p_{0^\circ\,C.},$$

A. *Measurements with the helium thermometer of 108 cm³.*

§ 2. *The Thermometer.* The description of this thermometer with the corresponding manometer can be found in Comm. N⁰. 152*a* [1]).

The evacuation of the reservoir and connected filling tubes required a great deal of time. While heating the reservoir to 250—300° C. a condensation pump was applied for 7 or 8 hours a day. It was not till after 10 days that the reservoir was entirely free from gas. Before the real filling, first the tubes and then the reservoir were rinsed with dry heliumgas.

The helium was taken from a cylinder of compressed helium produced from liquid helium. Before entering the thermometer, the heliumgas passed through a spiral placed in liquid air, so as to eliminate the last traces of moisture.

The reservoir, marked T_3, is made of Jena glass 16^{III}. Formerly with this reservoir frequently had already been measured. The dimensions as given by VAN AGT [2]) were: volume of reservoir $V_0 = 108.267$ cm³., glass capillary up to the wider part 45 mm³., change in volume of the reservoir due to difference of internal and external pressure: 4.625 mm³. for a difference of pressure of 75.26 cm. mercury. The volume of the steel capillary we measured 459 mm³.

The volume between the horizontal plane through the top of the adjustment-point to the end of the steel capillary we determined volumenometrically as given in Comm. N⁰. 164 § 4. The total noxious volume, up to the horizontal plane mentioned above, is 761 mm³.

It was further necessary to measure the volume of the space between the horizontal plane through the adjustment point and the mercury

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cf. Leiden Suppl. N⁰. 23, equation (137), the following values of $B_{100° C.}$:

$76\,p_0$	0° — 100° C. α_v	0° — 100° C. α_p	$B_{100° C.}$
111.6 cm	0.0036600	0.0036581	$+ 0.35 \times 10^{-3}$
52.1	36599	36603	$-$ 0.16
110.3	36601	36582	$+$ 0.36
76.0	36598	36591	$+$ 0.19
50.5	36595	36589	$+$ 0.29

Compare with this Leiden Suppl. N⁰. 51*a*, table I. Neither does the value for $B_{0° C.}$ measured directly by HENNING and HEUSE correspond to that of other experimenters. cf. the table quoted above.

[1]) P. G. CATH and H. KAMERLINGH ONNES. These Proc. 20, 991, 1155, 1917. Comm. Leiden N⁰. 152*a*.

[2]) Earlier calibrations see Comm. Leiden N⁰. 152*a* p. 10, note 4, and Comm. Leiden N⁰. 164 p. 19.

meniscus. This volume consists of a cylindrical portion and the residual volume, i.e. the volume between the meniscus and the horizontal plane carried through the top of the meniscus. This residual volume was calculated by means of the data given by J. PALACIOS [1]).

The expansion coefficient for Jena glass 16^{III} between 0° and 100° C. was determined at our request by Miss A. F. J. JANSEN by the weight-thermometer method. Measurements
with a vessel of 100 cm³. yielded $10^{-7} \times 243.2$ and 242.6 mean 242.9
„ „ „ „ 300 „ „ „ 242.0 „ 241.7 „ 241.8^5

mean $10^{-7} \times 242.4$

As expansion coefficient of mercury we took $10^{-7} \times 1826.0$. For our calculations we took as expansion coefficient for Jena 16^{III} 0.00002420 [2]).

§ 3. *Measurements of the pressures.* The pressure of the gas in the thermometer, apart from a few corrections, was determined by the difference of height of the mercury meniscus in the two manometer tubes, increased by the pressure above the mercury in the long manometer tube. This pressure was again determined by a mercury barometer placed beside the manometer. A correction was made for the difference of level between the barometer and the manometer. The corrections for the capillary depression were borrowed from DE HAAS—LOHNSTEIN's data [3]). The differences of the level in the mercury menisci were read by means of a comparator calculated upon a difference of height of 1.50 M., provided with three telescopes from an invar scale of 1.50 M. length divided into mm. The scale, comparator and telescopes were furnished by the Société Genevoise.

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1) J. PALACIOS. Trabajos del laboratorio de investigaciones fisicas, N⁰ 61. Annales de a Soc. Esp. de Fis. y Quim. **27**, 275, 1919. Cf. International Critical Tables Vol. I, p. 72.

2) Earlier values:

WIEBE and BÖTTCHER, ZS. f. Instr.kde **10**, 233, 1890:	240×10^{-7}.
PULFRICH, see SCHOTT, Vortrag Ver. z. Bef. des Gewerbefl., Berlin 1892:	240,6 × „
KAMERLINGH ONNES and BOUDIN, Comm. Leiden N⁰ **60**, 1900:	242 × „
SCHEEL, ZS. f. Phys. **5**, 257, 1921:	242,4 × „
VAN AGT and KAMERLINGH ONNES, Comm. Leiden N⁰ 176ᵃ, 1925:	235,5 × „

[For the formula given in Comm. N⁰. 176*a* for the thermal expansion of Jena-glass 16^{III}, the following coefficients are in better agreement with the experimental results, than those mentioned there:

$$a = 702.6 \qquad c = 19.39$$
$$b = 47.54 \qquad d = 14.31.$$

Added in the translation].

3) W. J. DE HAAS. Thesis Leiden 1912, p. 52. It does not seem necessary to make a recalculation on the basis of the measurements recently published by the P. T. R. (Zs. f. Instrumentenkunde **47**, 324, 1927). Seeing that it is here always a matter of differences, the alterations it would cause in each pressure reading would be below, except in a few unfavourable circumstances even far below 0.03 mm., which lies within the limit of accuracy finally arrived at.

§ 4. *The icepoint.* For this finely planed ice [1]) of distilled water was used carefully prepared with our own freezing apparatus. The thermometer was placed in a large flower pot filled with ice, which was carefully packed round the reservoir and the stem. During the measurements the ice was constantly kept in close contact with the thermometer. The ice was kept well moistened by regularly pouring distilled water upon it. The water that ran off was collected in an earthenware saucer, from which it escaped through an opening at the side [2]).

The variations in the reading registered by a BECKMANN thermometer placed in ice at a small distance from the thermometer reservoir for one day, and also the differences on different days, amounted to only a couple of thousandths of a degree.

The glass capillary is placed in ice to 10 cm. below the soldering place of the steel capillary.

§ 5. *The steampoint.* The steam apparatus, described by KAMERLINGH ONNES in Comm. N⁰. 27 [3]) has since undergone some changes, see fig. 1. The steam, after having passed by the thermometer reservoir *Th* and through the protecting mantle, is again condensed in a brass pipe *K* surrounded by a cooler, while the brass pipe reaches to within a few cm. of the bottom of the boiler.

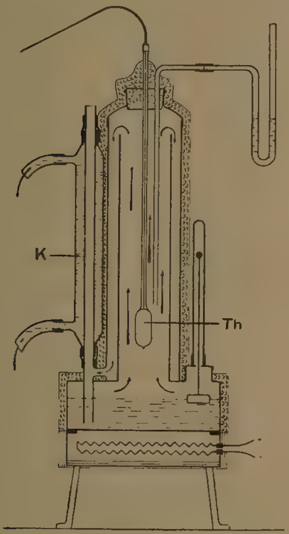

Fig. 1.

Gas is replaced by electricity for heating the water. This gives a more even temperature in the room and consequently in the mercury column in barometer and manometer.

The thermometer hangs in the vapour apparatus to within 10 cm. of the soldering place of the capillary. The protruding portion of the capillary is insulated by asbestos cord, to prevent the soldering place of Wood metal at the top of the glass capillary from getting hot.

To ascertain the pressure in the boiler a glass tube bent at right angles is introduced, one limb of which reached to the thermometer reservoir. The other limb, which is closed during the measurements can be brought into communication with an open water manometer by means of an india rubber tube. The air column above the water, which, when examining the pressure, is connected to the vapour in the boiler prevents the steam from condensing there, so that the manometer can be read off at ease for some minutes.

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[1]) A description will shortly be published of the rotating motor-driven ice-plane made by the Kon. Ned. Grofsmederij at Leiden, which has replaced the apparatus described by KAMERLINGH ONNES in Versl. Kon. Akad. v. Wet. Amsterdam Mei 1896, Comm. Leiden N⁰. 27.

[2]) Cf. H. KAMERLINGH ONNES, Comm. N⁰. 27 § 7.

[3]) H. KAMERLINGH ONNES, Comm. N⁰. 27 § 8.

The pressure in the boiler is regulated by the cooler. During the measurements the over-pressure amounted to 1 mm. water. This was taken into consideration in determining the temperature. The height of the barometer at each observation was given by the barometer that also gave the air pressure above the long tube of the manometer.

The pressure of the water vapour was reduced to international atmospheres by means of the factor 1.00062 [1]). The boiling point was calculated according to the table in LANDOLT—BÖRNSTEIN.

§ 6. The calculation of the pressure coefficient was made as described in Comm. N⁰. 156*a* § 3.

§ 7. *Results.* The ice point was observed on March 19th and June 3rd 1927. On the former day the following results were obtained :

H_0 = 986.482 mm.
.495
.467
.531 (water poured over the ice)
.531
.631 (a lot of water)
Accepted : 986.631 mm.

On June 3rd the melting water which ran off was regularly supplemented by pouring on distilled water. The measurements were :

H_0 = 986.619 mm.
.667
.662
.664
.662
.662
.655
mean : 986.656 mm.

For calculating the pressure-coefficient the mean of the two above values was taken : H_0 = 986.644 mm.

The steampoint was observed on March 16th and May 24th and 30th. The results are brought together in the following table. The 4th column contains the pressure coefficient deduced from each measurement, the last the mean of each day.

It appears that the greatest deviations occurred on May 30th, which no

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[1]) Suppl. Comm. Leiden N⁰. 51*a* § 3.

TABLE I.

Date 1927	H_{100} mm	Boiling point °C.	0 — 100° C. α_v	Mean
16 March	1349.233	100.377	0.00366118	
„	.216	.373	115	
„	.235	.377	119	
„	.227	.377	111	
„	.224	.377	108	0.00366114
24 May	1348.805	100.254	0.00366134	
„	.786	.253	118	
„	.829	.258	143	
„	.805	.259	115	
„	.816	.258	130	
„	.804	.257	121	
„	.758	.251	097	
„	.760	.250	102	0.00366120
30 May	1347.689	99.948	0.00366122	
„	.677	.945	120	
„	.670	.937	144	
„	.673	.937	147	
„	.594	.926	107	
„	.628	.923	152	
„	.587	.919	126	
„	.561	.904	155	0.00366134

doubt is connected with the fact that, owing to a change in the barometer height, the boiling point had considerably changed.

As general mean we found :

0.00366124.

B. *Measurements with the helium thermometer of 355 cm³.*

§ 8. KAMERLINGH ONNES and BRAAK [1]) agreed that for a more accurate determination of the pressure coefficient between 0° and 100° C. a thermometer of 300 cm³. was desirable. In this case the proportion of noxious space to the volume of the reservoir would be more favourable and therefore the influence of uncertainties in the size and temperature of the noxious volume upon the results would be smaller. This proportion comes to 0.0030 for measurements with the thermometer of 355 cm³. as compared to 0.0080 with those of T_3.

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[1]) These Proc. **10**, Nov. 1907, p. 429, Comm. Leiden N⁰. 101*b*, p. 14 note 3.

With a larger reservoir, moreover, the proportion of the surface to the volume is also more favourable, so that a possible surface effect will have less influence.

The diameter of the manometer tube of this thermometer was also taken larger (18 mm.) by which the uncertainties in the capillary depression were decreased [1]).

Finally, for the pressure determinations with this thermometer a single manometer was used, instead of manometer and barometer, as had always been used in the former measurements [2]). This eliminated the necessity of the reading of two mercury menisci [3]).

§ 9. The arrangement of the thermometer and corresponding manometer was as in Comm. N⁰. 152*a* to which we refer. The connection of the long manometer tube with the reservoir in ice was no longer necessary. In place of this a second tube filled with charcoal was introduced, which was used for further evacuation after the first tube.

§ 10. *Calibrations.* Reservoir (Tg_1) and glass capillary were calibrated with mercury. The result was (at 0° C.) :

Volume of reservoir from 3 weighings 355.173 cm³. ± 0.79 mm³.

Volume glass capillary between two marks from 5 measurings 39.56 ± 0.42 mm³.

With a difference of internal and external pressure of 770 mm. the change in volume in the reservoir was 21.58 mm³.

The reservoir and the capillary were made of Jena glass 16^{III}.

The volume of the steel capillary from 7 calibrations with mercury was found to be 503.67 ± 0.47 mm³.

The section of the short tube of the manometer at the adjustment-point was measured with mercury : Result of 4 measurings : 278.85 ± 0.18 mm².

The section of the long tube of the manometer was also measured with mercury at various important points. For the radius as mean of 6 measurings was found 9.22 ± 0.003 mm.

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[1]) The inaccuracies in pressure readings due to this are actually less than 0.01 mm. (cf. note 3 p. 972). The disadvantage that the volume at the adjustment point becomes greater is exceeded by this advantage.

[2]) This was made possible by the fact that the grant, made to us by the International Education Board enabled us to acquire the comparator and invar-scale mentioned in § 3.

[3]) On the other hand, if there is a temperature gradient in the room the differences of temperature in the mercury become greater. It appeared to be possible, however, to keep the difference of temperature at the top and the bottom of the mercury column between 0.08 and 0.02 of a degree.

§ 11. *The filling of the thermometer.* This was done in the same way as T_3 (§ 2). The evacuation of the reservoir, however, required considerably more time. After daily pumping had been going on for four weeks and the Mac Leod still registered pressure every morning, the thermometer, after being again evacuated, was put aside for a few months. When after 3½ months the pressure was again tested, it appeared that this had by no means increased in proportion to the time, whereupon the daily pumping was again begun. At the same time the reservoir was kept heated in an electric oven to ± 250° C. After pumping for a good week the Mac Leod showed no pressure in the morning.

The thermometer was filled with helium gas from the same cylinder as T_3.

§ 12. *The noxious volume.* As with T_3 the noxious volume between the adjustment-point and the soldering place of the steel capillary to the steel adjustment piece was determined volumenometrically. The steel capillary was placed for this in a copper tube, to keep the temperature constant. For this portion of the noxious volume between the adjustment point and the soldering place of the steel capillary to the steel adjustment piece was found (2 measurings) 410.62 ± 0.92 mm^3. The volume of the soldering place of the steel capillary to the glass capillary with the wider part of glass capillary was measured and calculated at 42.53 mm^3. The volume of the steel capillary (§ 10), 503.67 mm^3., added to this yields a total volume of 956.82 mm^3. up to the horizontal plane through the adjustment-point.

§ 13. *The measurements.* Concerning the measurements of the pressure we have only to say (see § 8) that two fixed telescopes could be used, as only two menisci had to be observed. The vacuum in the long tube of the manometer was maintained by a tube filled with charcoal regularly renewed and plunged into liquid air, and was kept under constant observation.

For the realizing of the ice- and steampoint we refer to § § 4 and 5.

§ 14. *Results.* The ice-point was determined on June 13th and July 5th:

June 13, 1927 :	974.110 mm.
	.188
	.191
	.180
	.181
mean	974.190 mm.
July 5, 1927 :	974.232 mm.
	.236
	.232
mean	974.233 mm.

For calculating the pressure coefficient the mean of these two values was taken: $H_0 = 974.211$ mm.

The results obtained by the determination of the steampoint, with the values for the pressure coefficient derived from it, are given in table II.

TABLE II.

Date 1927	H_{100} mm	Boiling point °C.	0° — 100° C. α_v	Mean
16 June	1331.448	100.162	0.00366100	
„	.423	.156	097	
„	.435	.154	117	
„	.317	.126	098	
„	.296	.120	098	
„	.266	.112	097	0.00366101
21 June	1331.416	100.147	0.00366112	
„	.394	.143	115	
„	.399	.139	134	
„	.391	.138	129	
„	.374	.135	124	
„	.372	.135	122	
„	.390	.135	140	
„	.387	.134	137	0.00366128
22 June	1331.924	100.283	0.00366147	
„	.920	.283	142	
„	.927	.283	149	
„	.888	.283	109	
„	.916	.283	138	
„	.915	.283	137	0.00366137
27 June	1330.320	99.845	0.00366104	
„	.322	.845	105	
„	.340	.848	107	0.00366107

As general mean 0.00366120 was found.

§ 15. *The fundamental pressure-coefficient for the international helium thermometer.* Taking into account the change of the fundamental pressure coefficient with the initial pressure [1]) the two series of observations yielded:

Thermometer reservoir	α_{iHe}
108 cm^3.	0.00366124
355 „	366119.

From this follows as mean : $\alpha_{iHe} = 0.00366121$, which may be rounded off as 0.0036612.

A correction must still be introduced on account of the circumstance that in the boiler (§ 5) the reservoir of the thermometer was not protected against the radiation of the bottom and against any superheated drops, spattering up. From measurements, intentionally taken therefor, whereat the temperature was read off from a Beckmannthermometer, which could be protected or not by a plate of tin, suspended horizontally beneath the reservoir of the thermometer, it appeared that at the same velocity of evaporation by which the measurements with the heliumthermometer took place, without a screen the temperature was 0.003 degrees higher than with a screen. Considering this, the result will be

$$\alpha_{iHe} = 0.0036611$$ [2]).

The remaining uncertainty in the result is due, except for accidental inaccuracies in observation, to a trace of uncertainty in the expansion coefficient of the glass [3]), and to that in the volume of the mercury menisci. Taking all factors together we should put the uncertainty at 2×10^{-7} at the most.

We may remark further that the value here found directly for α_{iHe}, within the limits of accuracy mentioned before, corresponds to the value, which was deduced from KAMERLINGH ONNES and BOUDIN's measurements for hydrogen and those by KAMERLINGH ONNES and CATH concerning the difference between hydrogen and helium (cf. § 1).

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[1]) Suppl. N⁰. 51*a* p. 20 equation (20).

[2]) This paragraph is added to the English translation in consequence of a kind remark of Prof. Dr. F. HENNING.

[3]) See p. 972 and the second note there.

Crystallography. — *On Quaternary Symbols of Zones.* By C. H. EDELMAN. (Communicated by Prof. G. A. F. MOLENGRAAFF.)

(Communicated at the meeting of September 24, 1927).

In crystallography the determination of zones causes no trouble, when we use a tri-axial system of co-ordinates.

If of a zone $[u_1\,v_1\,w_1]$ two faces are known $(h_1\,k_1\,l_1)$ and $(h_2\,k_2\,l_2)$ we have

$$\begin{aligned} u_1 &= k_1\,l_2 - l_1\,k_2 \\ v_1 &= l_1\,h_2 - h_1\,l_2 \\ w_1 &= h_1\,k_2 - k_1\,h_2. \end{aligned}$$

For a zone $[u_2\,v_2\,w_2]$ defined by the faces $(\bar{k}_1\,h_1\,l_1)$ and $(\bar{k}_2\,h_2\,l_2)$, whose symbols have been derived by a definite interchange and change of sign from those of the faces of the first bundle, we also have

$$\begin{aligned} u_2 &= h_1\,l_2 - l_1\,h_2 \\ v_2 &= k_1\,l_2 - l_1\,k_2 \\ w_2 &= h_1\,k_2 - k_1\,h_2. \end{aligned}$$

The symbol $[u_2\,v_2\,w_2]$ may, therefore, also be written $[\bar{v}_1\,u_1\,w_1]$, so that the second zone-symbol is derived from the first in the same way, in which the symbols of the second pair of faces have been derived from those of the first. This holds for all zones in general; e.g. the zone defined by the faces $(k_1\,h_1\,l_1)$ and $(k_2\,h_2\,l_2)$ is $[v_1\,u_1\,w_1]$; the one defined by the faces $(h_1\,\bar{k}_1\,l_1)$ and $(h_2\,\bar{k}_2\,l_2)$ is $[u_1\,\bar{v}_1\,w_1]$ etc. This property involves that corresponding ribs of a crystal get corresponding symbols, which needs must be so, considering the duality of faces and ribs.

Difficulties will arise, when one uses a tetra-axial system of axes and the faces are designated after BRAVAIS by symbols of four numbers or in general by four algebraic magnitudes.

To show this let us consider three zones:

$[u_1\,v_1\,q_1\,w_1]$ defined by the faces $(h_1\,i_1\,k_1\,l_1)$ and $(h_2\,i_2\,k_2\,l_2)$
$[u_2\,v_2\,q_2\,w_2]$,, ,, ,, ,, $(\bar{k}_1\,\bar{h}_1\,\bar{i}_1\,l_1)$,, $(\bar{k}_2\,\bar{h}_2\,\bar{i}_2\,l_2)$
$[u_3\,v_3\,q_3\,w_3]$,, ,, ,, ,, $(i_1\,k_1\,h_1\,l_1)$,, $(i_2\,k_2\,h_2\,l_2)$

The symbols of the faces belonging to the second (resp. third) zone can be derived from those of the faces of the first (resp. second) zone, by replacing the three horizontal indices by their opposites and then interchanging them cyclically.

The faces of the first zone can be made to co-incide with those of the second (resp. third) by a revolution of 60° (resp. 120°), in positive sense, round the crystallographical principal axis. Only for the sake of symmetry we shall also consider the third zone.

Application of the ordinary algorithmus, after provisional omission of the third index, gives :

$$\begin{array}{lll} u_1 = i_1\, l_2 - l_1\, i_2 & v_1 = l_1\, h_2 - h_1\, l_2 & w_1 = h_1\, i_2 - i_1\, h_2 \\ u_2 = l_1\, h_2 - h_1\, l_2 = v_1 & v_2 = k_1\, l_2 - l_1\, k_2 = v_1 - u_1 & w_2 = k_1\, h_2 - h_1\, k_2 = w_1 \\ u_3 = k_1\, l_2 - l_1\, k_2 = v_1 - u_1 & v_3 = l_1\, i_2 - i_1\, l_2 = -u_1 & w_3 = i_1\, k_2 - k_1\, i_2 = w_1 \end{array}$$

The ternary symbols now obtained are again complemented to quaternary ones by availing ourselves of the property that the sum of the three horizontal indices = 0. The symbols of the three zones are then successively :

$$\begin{array}{l} [\ (u_1) \quad (v_1) \quad (-u_1 - v_1) \quad (w_1)\ ] \\ [\ (v_1) \quad (v_1 - u_1) \quad (u_1 - 2\, v_1) \quad (w_1)\ ] \\ [\,(v_1 - u_1) \quad (-u_1) \quad (2\, u_1 - v_1) \quad (w_1)\ ] \end{array}$$

The relation that existed between the symbols of the corresponding faces of the zones is no longer present in the same form in the zone-symbols.

So in this symbolism — the one most applied — (GROTH, DANA, TSCHERMAK and others) corresponding zones do not get corresponding symbols. Strictly speaking this could hardly be expected, because in our deduction the third index occupies a very exceptional position. In searching for another symbolism, that fulfils the requirement of correspondency, we shall have to find a method, in which the three horizontal indices will be treated in the same way.

The ternary symbol has been found after provisional dropping of the third index ; provisional omission of the second or the third index gives other symbols. The symbols found in these three ways have been tabulated below :

Symbol of the	After omission of the	1^0 index	2^0 index	3^0 index	4^0 index
1^0 zone	3^0 index	u_1	v_1	—	w_1
	2^0 index	$u_1 - v_1$	—	$-v_1$	w_1
	1^0 index	—	$v_1 - u_1$	$-u_1$	w_1
2^0 zone	3^0 index	v_1	$v_1 - u_1$	—	w_1
	2^0 index	u_1	—	$u_1 - v_1$	w_1
	1^0 index	—	$-u_1$	$-v_1$	w_1
3^0 zone	3^0 index	$v_1 - u_1$	$-u_1$	—	w_1
	2^0 index	v_1	—	u_1	w_1
	1^0 index	—	$-v_1$	$u_1 - v_1$	w_1

We have thus found two values for every horizontal index.

By addition of indices belonging together we can compose a symbol for every zone, to which the horizontal indices of the face symbols have equally contributed. This addition yields for the three zones the symbols:

$$\begin{array}{l}
[(2u_1 - v_1) \quad (2v_1 - u_1) \quad (-u_1 - v_1) \quad (3w_1)] \\
[\ (u_1 + v_1) \quad (v_1 - 2u_1) \quad (u_1 - 2v_1) \quad (3w_1)] \\
[(2v_1 - u_1) \quad (-u_1 - v_1) \quad (2u_1 - v_1) \quad (3w_1)]
\end{array}$$

The correspondency of the indices of the three zone-symbols is, indeed, completely the same now as was the case with the symbols of the faces we started from, so the requirement of correspondency has been fulfilled.

WEBER [1]) has arrived at the same symbol along quite another way. Now the question occurs to us whether the result obtained, is the only solution of the problem. We shall, therefore, formulate the problem as follows:

To convert the ternary symbols of corresponding zones, obtained with the ordinary algorithm, into such quaternary symbols that these symbols present the same dependence as those of the corresponding faces that define the zones.

This, then, comes to a conversion of the numerical pairs:

$$\begin{array}{ccc}
u_1 & , & v_1 \\
v_1 & , & v_1 - u_1 \\
v_1 - u_1 & , & -u_1
\end{array}$$

in numerical triads:

$$\begin{array}{ccccc}
x & , & y & , & z \\
-z & , & -x & , & -y \\
y & , & z & , & x
\end{array}$$

in which the three unknowns x, y and z are bound by the relation:

$$x + y + z = 0.$$

The numbers x, y and z of the first triad have to be derived by a transformation to be discussed presently from the numbers u_1 and v_1 of the corresponding pair. So we can write:

$$\begin{array}{l}
x = f(u_1\ ,\ v_1) \\
y = F(u_1\ ,\ v_1).
\end{array}$$

But the same transformation must produce the numbers of the second triad from those of the second pair:

$$\begin{array}{l}
-z = f(v_1\ ,\ v_1 - u_1) \\
-x = F(v_1\ ,\ v_1 - u_1)
\end{array}$$

Likewise for the third set:

$$\begin{array}{l}
y = f(v_1 - u_1\ ,\ -u_1) \\
z = F(v_1 - u_1\ ,\ -u_1)
\end{array}$$

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[1]) Zeitschr. f. Krist. 57 (1922), p. 200 sqq.

When confining ourselves to linear transformation, we can write :

$$\begin{aligned} x &= a_1 u_1 + b_1 v_1 + c_1 \\ y &= a_2 u_1 + b_2 v_1 + c_2 \\ -z &= a_1 v_1 + b_1 (v_1 - u_1) + c_1 \\ -x &= a_2 v_1 + b_2 (v_1 - u_1) + c_2 \\ y &= a_1 (v_1 - u_1) - b_1 u_1 + c_1 \\ z &= a_2 (v_1 - u_1) - b_2 u_1 + c_2 \end{aligned}$$

The equations thus obtained are dependent, so that after elimination of x, y and z, they furnish only two equations :

$$\begin{aligned} u_1 (a_1 - b_2) + v_1 (b_1 + a_2 + b_2) + c_1 + c_2 &= 0 \\ u_1 (a_2 + b_1 + a_1) + v_1 (b_2 - a_1) + c_2 - c_1 &= 0 \end{aligned}$$

These equations of course admit of an infinite number of solutions ; but we are interested only for those that are independent of fortuitous values of u_1 and v_1, in other words those we obtain by considering the two equations as identities. This yields the relations :

$$\begin{aligned} a_1 - b_2 &= 0 \\ a_2 + b_1 + b_2 &= 0 \\ c_1 + c_2 &= 0 \\ c_2 - c_1 &= 0 \end{aligned}$$

The additive constants appear to become = 0. However, only two relations exist between the four co-efficients a_1, b_1, a_2 and b_2, so that an infinite number of solutions still will satisfy.

These considerations may still be extended by applying them also to the case in which the second, resp. the first index has been omitted. This furnishes some more relations, namely :

After omission of the second index :

$$\begin{aligned} x &= a_3 (u_1 - v_1) - b_3 v_1 + c_3 \\ y &= a_4 (u_1 - v_1) - b_4 v_1 + c_4 \\ -z &= a_3 u_1 + b_3 (u_1 - v_1) + c_3 \\ -x &= a_4 u_1 + b_4 (u_1 - v_1) + c_4 \\ y &= a_3 v_1 + b_3 u_1 + c_3 \\ z &= a_4 v_1 + b_4 u_1 + c_4 \end{aligned}$$

from which we can derive :

$$\begin{aligned} a_4 &= b_3 \\ c_3 = c_4 &= 0 \\ a_3 + b_3 + b_4 &= 0 \end{aligned}$$

And after omission of the first index :

$$\begin{aligned} x &= a_5(v_1 - u_1) - b_5 u_1 + c_5 \\ y &= a_6(v_1 - u_1) - b_6 u_1 + c_6 \\ -z &= -a_5 u_1 - b_5 v_1 + c_5 \\ -x &= -a_6 u_1 - b_6 v_1 + c_6 \\ y &= -a_5 v_1 + b_5(u_1 - v_1) + c_5 \\ z &= -a_6 v_1 + b_6(u_1 - v_1) + c_6 \end{aligned}$$

from which follows :

$$\begin{aligned} & a_5 = b_6 \\ & c_5 = c_6 = 0 \\ & a_5 + b_5 + a_6 = 0 \end{aligned}$$

The twelve co-efficients $a_1 \ldots\ldots b_6$ are, with the exception of the relations already found, not independent. This is shown best when we write the symbol of one of the zones three times now :

FIRST ZONE.

	1^0 index	2^0 index	4^0 index
1^0 symbol	$a_1 u_1 + b_1 v_1$	$a_2 u_1 + a_1 v_1$	w_1
2^0 symbol	$a_3 u_1 + b_4 v_1$	$b_3 u_1 + a_3 v_1$	w_1
3^0 symbol	$a_6 u_1 + a_5 v_1$	$b_5 u_1 + a_6 v_1$	w_1

This gives the relations :

$$\begin{aligned} & a_1 = a_3 = a_6 = b_2 \\ & b_1 = b_4 = a_5 = b_6 \\ & a_2 = b_3 = b_5 = a_4 \end{aligned}$$

The dependence of the twelve co-efficients $a_1 \ldots\ldots b_6$ is to be represented schematically as follows :

$$\begin{array}{ccccccc} a_2 & + & b_1 & + & b_2 & = & 0 \\ \| & & \| & & \| & & \\ b_3 & + & b_4 & + & a_3 & = & 0 \\ \| & & \| & & \| & & \\ b_5 & + & a_5 & + & a_6 & = & 0 \\ \| & & \| & & \| & & \\ a_4 & + & b_6 & + & a_1 & = & 0 \end{array}$$

The extension appears not to involve restrictions. So there is an infinite number of general transformations to derive quaternary symbols possessing the property of being correspondent for corresponding zones, from the ternary symbols of zones, obtained in the ordinary way, and defined by faces designated by BRAVAIS symbols.

As a matter of course the symbol composed above satisfies these relations:

$$a_1 = b_2 = 2$$
$$a_2 = b_1 = -1$$

while the symbol proposed by VIOLA [1]) which corresponds with:

$$a_1 = 1$$
$$b_2 = -1$$
$$a_2 = b_1 = 0$$

does not satisfy and consequently is to be discarded.

Now to which of the numberless possible symbols have we to give preference? It is evident that arithmetically no conclusive answer can be given to this question. Other requirements should be added to that of correspondency.

But there is one more point of view from which the problem of these symbols of zones can be generally studied.

If we define two faces by MILLER's symbols, the equation of the intersection-line is easy to find. It is:

$$x : y : z = au : bv : cw,$$

in which u, v and w have the ordinary value attached to them before, and in which a, b and c represent the lengths of the axes. Geometrically u, v and w can now be interpreted as the co-ordinates of a point of the zone-axis, if the three co-ordinates are measured by the concerned axial ratio as unit.

When we apply this principle to the case of a hexagonal system of axes, then it is clear that the ternary symbol, obtained in the usual way, can be interpreted geometrically in the way stated above.

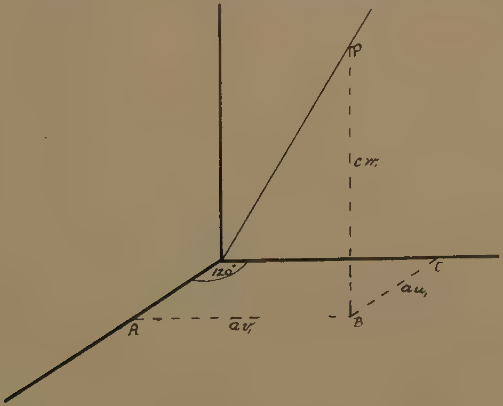

Fig. 1.

A point of the zone-axis can, therefore, be found by marking off au_1

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[1]) Zeitschr. f. Krist. **46** (1909), p. 345 sqq.

along the first axis, then av_1 parallel to the second axis, then cw_1 // the fourth axis (fig. 1).

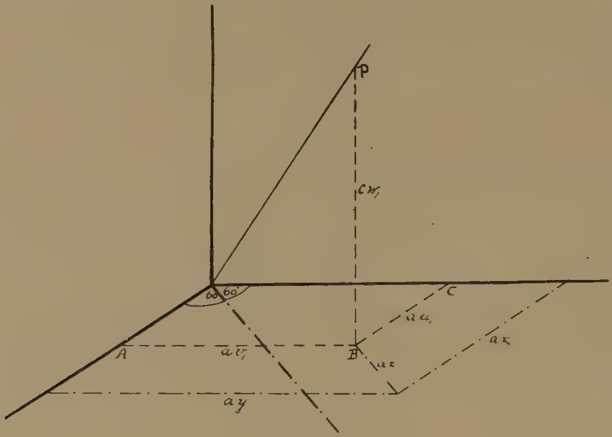

Fig. 2.

If we want a quaternary symbol and require the symbol to admit this geometrical interpretation, the point B must be reached after setting out the three distances (fig. 2). From the figure follows:

$$x - z = u_1$$

$$y - z = v_1$$

If we take

$$x + y + z = 0,$$

then we get

$$z = -\frac{u_1 + v_1}{3}$$

$$x = \frac{2\,u_1 - v_1}{3}$$

$$y = \frac{2\,v_1 - u_1}{3}$$

So in this way we get a conclusive result, viz. the same symbol that was found above and satisfies the requirement of correspondency, as shown already.

In fine it may still be observed that the same symbol is also obtained when converting the symbols after BRAVAIS into those obtained after MILLER, and by subsequently applying the algorithm and substituting the thus obtained ternary symbol by help of the known transformations by a quaternary symbol again. It would seem then that in this symbolism all advantages are combined and therefore it deserves to be generally received.

Summary.

1⁰. The problem of composing quaternary symbols that are correspondent for corresponding zones admits of numberless solutions.

2⁰. By an extension of the ordinary algorithmus one of the solutions can be found.

3⁰. The symbolism after VIOLA cannot be received.

4⁰. The symbolism after WEBER deserves general application.

Finally I wish to express my heart-felt obligations to Prof. J. A. GRUTTERINK m.e. for encouraging me to start these observations, and for his kind suggestions.

(From the Laboratory for Mineralogy of the Technical University of Delft.)

Mathematics. — *Representation of a Bilinear Congruence of Conics.*

By Prof. JAN DE VRIES.

(Communicated at the meeting of October 29, 1927).

1. A congruence $[k^2]$ of conics is called bilinear, if an arbitrary point of space defines one conic k^2 and an arbitrary straight line is a chord of one k^2. Evidently the planes of the conics pass through one fixed point O and form, therefore, a sheaf. Accordingly a line s through O is a chord of ∞^1 conics (*singular line*); these form a cubic surface Σ^3. This contains 5 pairs of lines that belong to $[k^2]$.

The surfaces Σ_1^3 and Σ_2^3 corresponding to the lines s_1 and s_2, have the k^2 in the plane $s_1 s_2$ in common. Any point S of the curve σ^7 which they have besides in common, carries a k^2 that cuts s_1 twice and a k^2 that cuts s_2 twice; accordingly through S (*singular point*) there pass ∞^1 conics.

The surface Σ^3 defined by the line OS, has a *double point* in S. This holds especially for the surface Ω^3 through the conics containing O.

The plane of any k^2 passes through O and cuts σ^7 in *six* more points; these lie on k^2.

2. In order to arrive at a *representation* of the congruence we shall consider two lines a_1 and a_2 chosen at random as directrices of a congruence of rays; this contains one chord b of a k^2; the transit B of b through a fixed plane β is considered as image of the k^2.

A point B of β usually carries one transversal b of a_1 and a_2 and is, therefore, the image of the k^2 lying in the plane Ob.

The conic k_0^2 that has the transversal b_0 in β as chord, is represented in the point range (B_0) of b_0.

The transit A_1 of a_1 is *singular* for the representation; the lines that join A_1 to the points of a_2, are chords of the conics that cut OA_1 twice and, consequently, form a surface Σ^3. Analogously A_2 (transit of a_2) is *singular*.

The transversal a of a_1 and a_2 through O is a chord of ∞^1 k^2; this is represented in the transit A of a; accordingly also A is *singular*.

3. The *conics* that have a straight line s as *chord*, are represented by the rays of the scroll with directrices s, a_1 and a_2. Their images form, therefore, a conic β^2 through A_1, A_2 and A (one of these k^2 passes through O).

Any β^2 through A_1, A_2 and A is the image of a system of conics that have a line s as chord. For if we choose two points B_1 and B_2 on β and if through these points we draw the transversals b_1 and b_2, the line of intersection s of the planes Ob_1 and Ob_2 defines the system of the k^2.

Two curves β^2 have one point B in common besides the singular points; it is the image of the k^2 lying in the plane $s_1 s_2$.

4. The *point range* (B) on a line c of β is the image of a system Γ of conics each of which has a transversal of c, a_1 and a_2 as chord. As these chords form a scroll, their planes *touch a quadratic cone* with vertex O.

Hence through a point S there pass two k^2 of Γ; on the surface of the conics of this system σ^7 is a *nodal curve*. The intersection of this surface with a surface Σ^3 consists, therefore, of the curve σ^7, to be counted twice, and of the two k^2 that are represented in the points of intersection of c and the β^2 defined by Σ^3. Consequently c is the image of a *surface* Γ^6.

5. Let Λ be the surface formed by the k^2 that cut a given line l; as *double curve* it has the k^2 that cuts l twice.

The surface Σ^3 corresponding to a point S contains three k^2 resting on l; hence σ^7 is a *triple curve* on Λ.

The image curve λ of the system has a triple point in A. Also A_1 and A_2 are triple points, for AO_1 and AO_2 are chords of three conics that rest on l. Besides the points A, A_1 and A_2, λ has three points B in common with a curve β^2, the images of the k^2 of Λ that have the line s as chord. Accordingly Λ has an image curve λ^6 with *three triple points*.

Two curves λ^6 have nine points B in common; there are, therefore, 9 k^2 that rest on two lines l, and the *surface* Λ has the degree 9.

6. A plane φ is cut by $[k^2]$ in the pairs of an involution. The pairs on the rays of a plane pencil with vertex M lie on a curve μ^3. Four rays of this plane pencil are tangents of conics k^2; hence OM is a chord of four k^2 that touch the plane φ. The conic β^2 corresponding to OM contains, therefore, the image points B of four k^2 touching φ.

The image curve of the system of the k^2 that touch φ, has *quadruple points* in A_1, A_2 and A; it is, therefore, a φ^8.

Two curves φ^8 have 16 non singular points in common; there are, accordingly, 16 k^2 that touch two given planes.

A φ^8 has 12 points B in common with a λ^6; consequently the conics that touch φ, form a *surface* Φ^{12} with *quadruple curve* σ^7.

7. The *pairs of lines* belonging to $[k^2]$ form a scroll $\triangle$. As any surface Σ contains five of these pairs, the image curve δ of $\triangle$ has quintuple points in A_1, A_2 and A and any β^2 contains five more points B of δ. Accordingly the image curve is a δ^{10}. It has 15 non singular points in common with a λ^6; hence $\triangle$ is a *scroll* of the degree *fifteen.* Indeed, a line s cuts five lines of $\triangle$ in O and ten lines outside O.

Zoology. — *Observations on the adhesive apparatus and the function of the ilio-colonring in the living larva of Amphioxus in the growth-period.* By Prof. J. W. VAN WIJHE.

(Communicated at the meeting of September 24, 1927).

I. Adhesive apparatus.

In the November meeting of 1925 I reported on the occurrence of three papillae, partly observed also by others, at the anterior part of the larva of Amphioxus lanceolatus in its growth-period. Their presence has already been observed in the larva with a single gill-pouch. They get bigger during the larval growth, but perish as the metamorphosis advances. They secrete a mucous substance, which I suppose to be viscous.

The anterior papilla is unpaired, lies right in front of the mouth and is provided with glandular cells with flagellate threads, which carry its secretion product (together with that of the club-shaped gland) into the mouth. This will promote the formation of slimy strands in which the food-particles are captured.

The other two papillae are situated behind the mouth in the young larva. They form a pair: a right papilla and a left one.

During the larval growth-period the left papilla remains with its fore-part close behind the mouth, which ultimately extends caudally beyond the region of the 5th gill-slit. When the left pterygial fold appears just behind the papilla, the latter forms on this fold in caudal direction a long tape-like glandular stripe. This stripe does not reach the end of the pharynx, consequently it does not overlap that portion of the fold that in older larvae lies behind the pharynx.

In the course of the larval growth the right papilla also forms a long tape-like glandular stripe. This one is situated on the right pterygial fold. It extends about as far back as its antimere on the left fold. Its fore-part, however, does not shift caudally, but already in an early stage it grows rostrally as far as the basis of the ventral, rostral fin in the topographical median plane. This accounts for the fact that earlier authors maintained erroneously that the ventral rostral fin was continued caudally in the right side-fold.

Some authors suspected that the asymmetry of the larva is owing to the way in which it rests on the ground. They supposed the larva to lie on its side, just as the larva of the Pleuronectidae, of which the one eye, intended for the inferior side, migrates to the superior side, which contains the other eye. Analogously the left gill-slits of the larva of Amphioxus were supposed by these authors to migrate for a time to the right side.

Most adherents of this hypothesis assume a left lateral position of the larva. Of late years, however, the suggestion was made that the larva must lie on its right side.

But if my view be the right one, viz. that the two tape-like glandular stripes secrete a viscous matter by which the larva can affix itself for a time, then the larva does not lie on the bottom, but stands, as it were, on its pterygial folds. True, in that posture its sagittal axis is not vertical, but oblique, because ventrally the right and the left fold do not extend equally far. Whether the left- or the right side will incline towards the bearing surface, must depend on the fact whether the right or the left fold extends farthest ventral.

This changes with the age-period. In young larvae the left papilla lies in the topographical ventral median line, and the right papilla a little higher on the right side. Then the larva must incline the fore-part of its body dextrad. But later on, when the right pterygial fold reaches farther down than the left one, the front-end of the larva must be turned obliquely towards the left.

The presence of the adhesive apparatus in the larva of Amphioxus would not only afford another point of agreement with the larva of Tunicata, but would also clarify the origin of the peribranchial cavity in Amphioxus.

Now was the time to watch the living larva, and to ascertain whether it can affix itself or not.

The Direction of the "Biologische Anstalt" in Heligoland accorded to me the privilege of working in its beautiful, and well-appointed, newly-built aquarium. For 11 days in the first half of last August I studied there the living larva. When I arrived there, 11 larvae were available. They were from 4 to 5 mm. in length and had from 13 to 15 (left) gill-slits. The atrium had not made its appearance yet; every trace of right gill-slits was lacking.

They were lying on the bottom of the big glass-jar where they had been deposited. When the water was stirred they swam for a short while performing eel-like windings, but soon they sank to the bottom again.

By help of the pipette, I transferred some into a shallow glass, so that they could be watched with the binocular microscope. All of them immediately sank to the bottom, some lay on their left, others on their right side. Sometimes it happened that a larva, that had been lying on the one side, turned on the other for resting.

When shaking the glass a little I observed that some larvae shifted bodily to other places, which proved that they had been free to move about. Of others, however the fore-part appeared to stick to the glass, as the posterior (the largest) portion of their body was swinging to and fro.

One day later, after the larvae had been set swimming in the big glass, I happened to see four times that one of them was hanging on the vertical glass-wall. It erected itself vertically with the rostrum turned upwards. On shaking the glass a little it appeared that, roughly estimated, $^1/_3$ of the body adhered to glass-wall, but the lower $^2/_3$ was swinging freely to-and-fro.

The contact lasted, however, only a short time, about one minute, then the animal freed itself by some powerful to-and-fro strokes of the caudal part, to sink down motionless, or to swim to the surface and thence to subside without moving.

The next day I received four newly caught larvae. Prof. HAGMEIER gave me a high rectangular cuvette with parallel walls of cut glass and a binocular microscope with BRAUS' stand, so that the microscope could be mounted horizontally. But I was not so fortunate as to see a larva on the vertical wall. This failure I ascribed to the smooth inner wall of the cuvette, on which hardly any material from the seawater could have been deposited, so that I expected a better result the next day. Such was the case; then I was soon able to show a larva suspended in the way described just now. But before we could mount the microscope, we saw the larva set itself free and subside to the bottom.

The existence of an adhesive apparatus was now sufficiently demonstrated, so that next I directed my attention to other functions of the living animal. The day before my departure from Heligoland all the larvae but two had perished. This was perhaps owing to inadvertency, as on preceding days I had refreshed the water from the tap, instead of drawing it directly from the sea.

But also the two living larvae were more dead than alive. They were still transparent and not white as the others, but they did not move even when the water was stirred. I put both in the high cuvette where they went down to the bottom. Now by help of a pipette I brought one of them to the surface of the water close to the glass-wall. Without moving at all the animal sank horizontally to the bottom. A second time I brought it up, with the same negative result. But the third time the animal remained hanging on the glass-wall after having descended half way; then it assumed a vertical position, rostral part upwards; on moving the cuvette the caudal end swung to-and-fro. Now the binocular microscope was mounted horizontally and the left side of the animal appeared to be turned to the glass-wall. Owing to the low magnification — also with the strongest objective systems [1] — we could not tell whether the left side of the larva was pressed against the glass-wall, or (as I suspected) whether the larva was only inclined to it at an acute angle. Several gentlemen working at the "Anstalt" could witness that the larva was hanging on the wall. When I looked at it again three hours later, it was of an opaque white and was dead. Infusioria were creeping with their cilia up-and-down the animal or were swimming round it. The next day it was still hanging there, but was hardly more than the skin. Its inside had been eaten up; of the intestines, even of the chorda nothing could be distinguished.

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[1]) The thickness of the glass-wall prevented us from observing the larva under the strong objective-lenses of a monocular microscope.

I purposely dwelt on these observations at some length, because they tended to establish the fact that in its growth the larva of Amphioxus is provided at its front-end with an adhesive apparatus. Nor can it reasonably be doubted that this apparatus (cf. my paper referred to at the outset) is supplied by the right-, and the left papilla of the young larvae, which grow in the older larvae as far as the glandular stripe on the right and the left pterygial fold.

Now let me discuss the origin of the peribranchial cavity in Amphioxus and Tunicata, which many authors hold to be homologous.

Origin of the peribranchial cavity in Amphioxus.

Our knowledge of the origin of the peribranchial cavity in Amphioxus we owe in the first place to LANKESTER and WILLEY (1890).

For many years already I have been collecting and cutting material to observe the origin of the pterygial folds and of the atrium. In this paper I shall give a brief report of my experience, which I intend to illustrate copiously in a later work.

The first foundation of the pterygial fold appears as a small eminence on the wall of the pharyngeal region just behind the homolateral adhesive papilla. Initially its caudal growth is but slow up to the termination of the pharynx. After this its growth is quicker, so that with 18 gill-pouches shortly before the metamorphosis it covers a long distance beyond the pharynx.

The left pterygial fold originates considerably later than the right one. It does not yet exist in a larva with 7 gill-slits [1]). As stated above it grows as far caudad as the right fold, but rostrally it does not grow so far, as it begins behind the mouth. The right fold on the contrary extends anteriorly up to the first gill-slit. Its apparent continuation up to the basis of the rostrum (in the topographical ventral median line) belongs to the right adhesive papilla.

Apparently the adhesive papillae have given the first impetus to the origin of the pterygial folds, which afterwards form the atrium. On this ground the papillae may be considered to be instrumental to the origin of the atrium.

In the first stage of the metamorphosis the right and the left pterygial folds coalesce behind the pharynx, but near their hinder extremity they leave a slit-shaped atrioporus open.

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[1]) HATSCHEK (Zoologische Wandtafeln, herausgeg. von Dr. R. LEUCKART Taf. 72 Acrania) gives an instructive picture of a larva with 7 gill-slits, but in his explanation (l.c. Fig. 12) he confuses the right side of the animal and the left one. He says that the fold lies on the left (read: right) side, and the gill-slits lie on the left (read: right) side but that afterwards they shift to the right (read to the left).

It is remarkable that in his explanation of Fig. 14 he says that the anus of the larva in Fig. 12 lies to the right, which is correct (anyhow for the presence of 1 to 6 gill-slits), whereas in the larva with one gill-slit (l.c. Fig. 10) the anus on the picture is on the left side, which again is not correct.

LANKESTER and WILLEY found that this intergrowth takes place postero-anteriorly; just the reverse direction is observed in the origin of the folds.

Towards the close of the first stage of the metamorphosis (after WILLEY 8 stages are distinguishable) the closing of the atrium is completed.

At first sight the direction of the formation of the atrium, and also of that of the pterygial muscle, is surprising, but a clue to it may be found, when the normal posture of the larva in rest is such that initially it is supported by its two adhesive papillae and afterwards by the glandular stripe of the pterygial folds. The folds form the side-walls of a longitudinal groove on the ventral side of the animal. The groove is closed by the object on which the animal rests so as to form a channel open behind. The row of the (left) gill-slits debouches into the groove, the bottom of which is turned upward.

The water that has served for respiration and feeding flows from the gill-slits into the channel, formed by the groove and the underlying object. It is transported further in caudal direction. In swimming there is no channel as the object is absent, and the groove is open over its whole length, unless its edges close up, which can often be seen on cross-sections. But this does not matter, as an apparatus for removing the used water from the vicinity of the mouth is not wanted, because the animal continually moves from one place to another.

In the resting larva the effect of this apparatus is increased when the metamorphosis has begun, because behind the pharynx the walls of the two pterygial folds, facing each other, get fused, thus forming the foundation of the atrium. Now in this region the pterygial muscle appears about simultaneously. Its contractions constrict the atrium, so that a sort of sipho arises, which will drive out the respiration water from the atriopore with greater force. The atrium now closes soon in anterior direction and the pterygial muscle grows in the same direction.

When the closure is accomplished the larva is provided with so powerful a respiratory organ (during swimming as well as during rest) that the gill-muscles will degenerate and ultimately disappear as the metamorphosis progresses. On the gill-slits of the right side, which do not appear before the closure of the attrium is completed [1]) muscles do not develop any more.

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[1]) FRANZ (1925) (Kap. II p. 427 sqq.) believes that already before the formation of the atrium gill-slits of the right side are open to the outside directly. He pictures (l.c. Table 16 Fig. 5) a transverse section from a series, that appears to have been studied rather cursorily. The two openings *r. ö* and *l. ö* are not right and left gill-opening, as is asserted in the explanation of the picture, but the double section of a left gill-slit curved through contraction;

end. c is not the section of the "Endostylcoelom" for the collapsed truncus arteriosus can be seen in its proper place (on the nether lip of the right boundary-fold, left side of the figure) in the shape of four cohering cells; *end. c* is the cavity of a (left) gill-arch with some fibres of the gill-muscle cut longitudinally. All visceral muscle fibres represented

Now the adhesive apparatus has become superfluous and degenerates.

Besides being a respiratory organ the atrium has still to perform another function, viz. the protection of the pharynx and the mid-gut. Now the larva can modify its habitat, and hide in the sand, without any harm being done to its gills, its liver or mid-gut and without any chance of the gills being stopped up. The numerous larvae in the 2d to the 8th stage of the metamorphosis, that I received from Naples, had all been caught from the sand.

Origin of the peribranchial cavity in Tunicata. A comparison with Amphioxus.

I shall be brief about it for two reasons: 1⁰ because I have but little experience of this origin in Tunicata, and 2⁰ because in 1914 (pp. 71—74) I reported already on the comparison between Tunicata and the young larva of Amphioxus.

In Ascidians the origin of the peribranchial cavity is quite independent of the adhesive papillae, while the pterygial folds do not occur in Tunicata. Consequently their peribranchial cavity cannot be homologous with that of Amphioxus, which originates in quite another manner.

I agree with VAN BENEDEN and JULIN (1886, pp. 401—405) in assuming.

1⁰. that in Acopa this cavity must be derived from the pair of gill-channels of Copelata (Appendicularians);

2⁰. (l.c.p. 387) that the strand of entoderm- cells, which in the larva of (Appendicularians and) Ascidians is found in the "tail", is the rudiment of the gut in the trunk of the larva of Amphioxus, so that the post-branchial gut in Tunicata must be a totally different part of the body from that in Amphioxus.

For the rest the comparison made by the authors of the larva of Ascidians and that of Amphioxus is untenable, also in consequence of subsequent researches.

It induced me (1914) to draw the following conclusions:

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in Fig. 5 belong to the gill-muscles, that disappear during the metamorphosis. The foundation of the pterygial muscles is still cellulous, not fibrous, and FRANZ's assumption (l.c. p. 430) that in the larva of Fig. 5 they should already possess muscle fibres, is erroneous.

He presumes to have to correct my observations, but I cannot accept his view. On *transverse* sections of an adult Amphioxus it can easily be seen that the plates of the pterygial muscles look freely into the narrow "abdominal channels" and in the lateral part of the side-channel. True, the lower border of those plates is not free everywhere but here and there attached to the skin, by which the "abdominal channels" have originated. In the medial part of the side-channel the lower border of the plates is attached in the trunk region to an outgrowth of connective tissue, which, however, is lacking more laterally. So this outgrowth forms merely an incomplete partition wall. Laterally there is a free communication between the groove of the side-channel with spaces between the muscle plates. A *sagittal* section may involve errors here and has led FRANZ (l.c. Fig. 8) astray in supposing the pterygial muscle to be composed of little cases closed all round.

1⁰. that morphologically the first pair of gill-slits, which in Amphioxus has been metamorphosed into mouth (tremostoma), and clubshaped gland, corresponds with the pair of gill-channels of the Appendicularians;

2⁰. that the postbranchial intestinal loop of Tunicata has to be looked for morphologically in the second pair of gill-slits of Amphioxus, of which only the left antimere occurs as the first gill-slit in the larva, but disappears during the metamorphosis, while there is not so much as a rudiment of the right antimere.

It might be possible, though, that in some Tunicata this very antimere should form the intestinal loop. On this matter I have now a more settled opinion.

The intestinal loop of Copelata namely lies to the *right* [1]) of the median plane, which passes through the spinal cord and the gl. thyroidea (the so-called "endostyl"). In Acopa on the other hand it is morphologically located to the *left* [2]) of that plane.

The term "Acopa" is defective, as it is indicative of the absence of a character (absence of a tail). With sharply distinguished positive characteristics Tunicata may be divided according as the intestinal loop lies to the left or to the right, into *Laevicolica* (= Acopa) and *Dextricolica* (= Copelata).

It may now readily be suspected that in the large group of Laevicolica the intestinal loop corresponds with the foremost (left) gill-pouch of the larva of Amphioxus, in the Dextricolica, on the other hand, with the right antimere of this pouch, which is no longer developed in Amphioxus. This difference may account for a large differentiation of Laevicolica. They are distributed over some orders and many families, whereas the differentiation of Dextricolica is restricted to at most two families, if Kowalevskia is to be considered as a representative of a separate family.

II. Swimming movements.

Many years ago I tried to interpret the remarkable asymmetry of the pharynx of the larva of Amphioxus, the disappearance of the primary mouth, its substitution by morphologically the first left gill-slit, and some more phenomena [3]) by advancing the hypothesis that the ancestors of Amphioxus had rotated "to the left" when they were swimming, round their long axis i.e. in the direction from right to left (along the ventral plane).

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[1]) In most Copelata also the anus lies on the right side. In Megalocercus and Stegosoma it lies in the median plane. If the suggestion expressed in the text be correct, it must originally have lain to the right in these two genera.

[2]) In Corellidae the intestinal loop lies to the right of the gill-basket, but DE SELYS LONGCHAMPS (1900) has found that in the larva the anus debouches into the foundation of the *left* atrium. The site of the intestinal loop on the right is, therefore, to be regarded as a secondary displacement.

[3]) Such as the absence of an organ of equilibration and of image-forming eyes. Afterwards also the initial location of the anal outlet on the right side of the body.

HATSCHEK (1881) observed this movement (which occurs also in the development of many Invertebrates) in the embryo, even for some time after it had disengaged itself from the egg-menbrane.

Now, when FRANZ (1924 p. 6) had found in most cases a similar rotation in the adult animal when swimming, I also expected it in the larva, but this expectation was not realized.

I could not note any rotation in the eel-like windings, alluded to above — observed already by LEUCKART and PAGENSTECHER (1858).

It still remains to be seen whether the hypothesis is in any way substantiated by the mode of moving of younger larvae than those that I had at my disposal.

Other authors have endeavoured to ascribe the asymmetry to the condition of rest. This, however, seems impossible to me, especially after what has been said above about the behaviour of the larva during rest.

I have to assume that in its period of growth the larva lies attached to objects on the bottom of the sea, mostly temporarily, but sometimes also detached from them, now on its left, now on its right side. At intervals it swims higher up, and is then carried along by the ocean-currents. From the second stage of the metamorphosis upward — when the atrium has been fully developed, it also hides in the sand; at intervals it leaves its hiding-place. The vertical posture of larvae suspending freely in the water, as described by WILLEY (1891) applies probably only to stages of the metamorphosis. All the larvae, living or dead that I observed in Heligoland sank motionless in *horizontal* posture to the bottom of the vessel.

III. Food transport.

The food is moved along the alimentary canal by the cilia, which, just as in the case of the full-grown animal, line the lumen of the intestinal canal over its whole length.

At the wheel-organ and the gill-slits, but also at the ilio-colonring the cilia have grown to long flagella, which form a living, brisk grating spectrum. Light causes in those two places two beautiful green spots, by which the larva of Amphioxus is recognizable [1]) among the many other larvae in the plankton. Muscular contractions were not observed at the intestine behind the pharynx. Indeed, muscle fibres are not known either in this part of the intestine of the larva.

In order to watch the progress of the food *a little* finely pulverized carmin was added to the water of the watchglass, in which a newly caught larva had been placed. It lay with the left side upward and had 15 gill-slits. The violent movement of the flagella of the wheel-organ caused the grains of carmin to be conveyed along the mandibular groove into the wide mouth-opening. The dorsal border of the groove had already been enlarged by the foundation [1]) of the left cheek that had just made its appearance, and which scarcely reached the front-end of the long, oval mouth-opening. A few grains flew up [2]) over the cheek-foundation; still, they got into the mouth-opening. While the organ set up a powerful current posteriorly, its violent undulatory movement was directed anteriorly.

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[1]) LEUCKART and PAGENSTECHER already (1858 p. 559) called attention to these spots. They say that the larvae "im Pokale leicht erkannt [werden] an der zartgrünen Färbung, welche diejenigen Stellen des sonst durchsichtigen Körpers auszeichnet, an welcher die Kiemen und jene, an welcher die hintern Partien des Darmes liegen. Sie sinken, wenn sie sich nicht bewegen, im Wasser unter".

The wheel-organ, seen in a side-view of the larva, presents the shape of a horse-shoe, with its open side turned caudally towards the mandibular groove. As the undulations of the threads in *either* limb [3]) of the horse shoe are directed anteriorly, the apparent wheel-like rotations of the apparatus are lacking, which JOHANNES MÜLLER (1841) has described at the extremities of the "finger-shaped figures" in the developed Amphioxus. At the top margin of such a figure he found the undulatory movement directed anteriorly, at the lower margin, on the other hand, it was directed posteriorly.

At the thick anterior border of the mouth-opening of our larva there was to be seen a bundle of long threads which quietly struck at the mouth at occasional short intervals. This bundle belongs to the unpaired mandibular papilla.

With a deeper focussing of the microscope HATSCHEK's groove revealed itself under the wheel-organ. On the bottom of the groove lay some small clusters of carmin-grains, that had got there accidentally. Here there seemed to be a perfect condition of rest, contrary to the violent movement at the border. Even after an hour the shape of the clusters had not altered appreciably.

At the gill-slits the undulation of the flagella could be seen beautifully. At the anterior border the direction of the undulation was dorsal, at the posterior border it was ventral. This is an opposite direction to that which JOHANNES MÜLLER has observed after the metamorphosis at the half-slits of the animal. He also observed that the wheel rotation is only a semblance, but that in reality the flagella expel the water in quite another direction viz. through the gill-slits.

The grains of carmin did not come out through the gill-slits — I had used a small quantity of carmin on purpose — but they had accumulated in the shorter or longer mucus-strands, which entered the alimentary canal at the end of the pharynx. This mucus is secreted by the pre-oral organ, the mandibular papilla, and also in the pharynx itself. Directly when the red strands entered the gut at the end of the pharynx, they began to glide linearly with uniform velocity towards the ilio-colonring which they soon filled up. Here the transport of food was stopped for some time, while the strand was being revolved round its axis by the long flagella that line the inside of the ring.

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[1]) The foundation of the cheek grows later on rostrally over the pre-oral organ (wheel-organ + HATSCHEK's groove) as well as caudally over the mouth-opening.

[2]) In the description we have tried to give an impression of the velocity as it appeared magnified by the microscope.

[3]) The left limb is shorter than the right one. It follows the lower border of the left lateral muscle and terminates near the posterior border of HATSCHEK's groove. The right limb reaches farther backward and presents on cross sections a strongly bent course. This curve is not very well observable in a side-view.

After some time part of the strand entered the rectum and moved on slowly in a straight line, while the portion left behind in the ring continued revolving. When the ring was empty the strand had filled up the whole rectum as far as the anus. Soon the strand was thrown out slowly piecemeal. All the time the animal had been lying quietly and turned over only once from its right side on its left.

When the gut was emptied the ring was of a light pink, which manifested resorption. But also the clubshaped gland had in some degree assumed this colour, for which the blood must have been responsible.

The experiments with carmin were repeated several days, also for the purpose of determining the time required by a strand to pass through the various sections of the alimentary canal. This time, however, appeared to depend on all sorts of conditions.

It differed e.g. according to the length of the strand that issued from the pharynx; also according as a strand was or was not followed soon by others; and according as the flagella in the ring beat briskly or tardily (the latter occurred sometimes in animals that had been caught several days ago).

In the above-described experiment the strands had filled the ring in two minutes; after a rotation of 5 minutes the ring was empty, and the whole rectum was filled, and after another 4 minutes the whole intestinal canal was empty, so the whole time-interval in the post-pharyngeal part of the alimentary canal amounted to 11 minutes.

After the intestine had been emptied a very small lump of carmin grains glided from the pharynx in one minute up to the ring, remained there quietly for one minute; when entering the ring it revolved for one minute and ultimately also passed through the rectum in one minute.

The same distance covered by a large amount of food in 11 minutes, was gone over, a short time later, by a very small quantity through an empty gut in four minutes.

These time-data can only serve for examples, yet with other larvae c.p. I obtained time-values, that differed little from the above.

If a fair quantity of food glided from the pharynx after the ring was already quite full, it first stopped before the ring, but subsequently it also partook of the rotation, I suppose because it had been sufficiently agglutinated with the contents of the ring. This affords the clue for the fact that the end of the mid-gut often exhibits a slight dilatation just in front of the ring.

During the comparatively slow linear movement in the rectum the food-strand was mostly broken to pieces, just as ANDREWS (1893) also observed in Asymmetron.

Time failed to experiment with other substances than carmin. Once I administered ammonium-carmin powder, which is easily soluble in distilled water, but appeared almost insoluble in sea-water. Contrary to my expectation its action was toxic. The ring was soon filled; the food began to revolve. This lasted about an hour! (55 minutes), then it entered the rectum in three several pieces, of which the hindmost appeared in the anus after 6 minutes. The front piece was not thrust out yet after 15 minutes. All that time the larva lay still, the right side uppermost. After a couple of hours the animal was markedly curved and dead; it still lay on its left side.

Function of the ilio-colon ring.

From the foregoing it follows that in the ring a complete mixture must take place of the ingested food and the digestive fluids. Moreover resorption takes place here for which there was no time [1]) in the mid-gut, because of the quick rate at which the foodstrands passed through it.

It can be said, therefore, that the ilio-colon ring in the larva of Amphioxus — presumably also in the full-grown animal — functions as a stomach, although morphologically it does not agree at all with the stomach of higher animals. For this stomach is a widened portion of the gut behind the oesophagus and before the embouchure of the efferent duct of the liver. In Amphioxus and its larva a stomach is absent in the corresponding place. But the ilio-colon ring lies on the border between mid-gut and rectum (end-gut) and corresponds morphologically in higher animals with part of the coecum, or with the appendix.

A coecum is found already in Selachians, but in Holocephali we find in its stead still a ringshaped glandulous piece of the gut.

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[1]) Time is available for it in some cases only in the hindmost part of the mid-gut. Also in the end-gut time is available.

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POSTSCRIPT.

Just when this paper had appeared in Dutch, FRANZ was so kind to send me his extensive works of this year on Amphioxus.

I cannot enter into them in detail and must confine myself to two points concerning the present paper.

1^0. I am happy that they drew my attention to the paper of J. H. ORTON: "On a Hermaphrodite Specimen of Amphioxus, with Notes on Experiments in Rearing Amphioxus", Journal of the Marine Biological Association of the United Kingdom, Vol. 10, 1913—'15.

In this paper ORTON (l.c. p. 511) already stated that larvae of Amphioxus, a fortnight old, when "only the first few gill-slits had appeared ...... stuck to the bottom of the vessel in the head region."

So ORTON was first in discovering the attachment of the larva to objects. But I cannot agree with his suggestion that this may occur by a secretion of the club-shaped gland, opening on the left side, and that "then the larva would be able to feed only from the right side of the body."

As we have seen, the feeding occurs just as well whether the animal is lying on the right or on the left side. Moreover, in my opinion, the very young attached larva will not lie on the left side, but seem to be resting on the right side, as noted above, p. 992.

2^0. FRANZ (Morphologie der Akranier, Ergebnisse der Anatomie und Entwicklungsgeschichte, Bd. 27, 1927, p. 593) figures a median section of a larva of Amphioxus with about 14 gill-pouches in the period of growth. The pre-oral organ is cut twice, showing two fossae, a foremost larger one, in contact with the notochord and behind this fossa, but more ventrally, a smaller one. FRANZ says (l.c. p. 594): "die grössere Grube wird zum Räderorgan, die kleinere zur HATSCHEK'schen Geisselgrube".

In a series of transverse sections, however, of a larva at this stage, one easily sees that the interpretation of FRANZ must be inverted: the anterior, larger fossa in contact with the notochord being the groove of HATSCHEK. The smaller posterior one, pushed away from the notochord is a part of the wheel-organ (Räderorgan). It is the deep curve of the longer, right limb of the horse-shoe mentioned above, p. 999 footnote.

The term "Geisselgrube" for the groove of HATSCHEK is a misnomer, as it shows no flagellation, at least not in the larva. The flagellate cells bordering the opening of the groove in front and at the sides [1]) belong to the wheel-organ.

The position of both fossae in a transverse section of a somewhat older larva (first stage of the metamorphosis) may be seen in LANKESTER and WILLEY (1890, fig. 13). Here (in the "praeoral pit") *s o* is the groove of HATSCHEK and *w o* the deep curve in the right or inferior limb of the horse-shoe noted above.

My sections show that this curve is straightened out during the period of metamorphosis. At the end of this period the "Flimmergrube" (which, 1901, I found in the adult, but is lacking in the larva) arises as an outgrowth from the posterior end of the groove of HATSCHEK. It is not a transformation of the "curve" as might erroneously be presumed and it does not arise from the wheel-organ.

Concerning its function in the adult I suggested (1901) that it would contribute in evacuating the mucus secreted by the groove of HATSCHEK. Probably the same function will be performed in the larva by the deep curve in the right arm of the wheel-organ (right limb of the horse-shoe).

Groningen, December 1927.

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[1]) Both arms of the wheel-organ (= limbs of the horse-shoe) uniting in front of the groove of HATSCHEK are prolonged rostrally (in the larve as well as in the adult) into an unpaired process.

Geology. — *The compacting pressure of sediments*. By J. VERSLUYS.

(Communicated at the meeting of October 29, 1927).

Attention was drawn in 1908 by H. C. SORBY (1, pp. 227—32) to the phenomenon that most sediments, according as they attain a greater depth, become more compressed, so that the volume of pores decreases. This is especially of effect for sediments that arise from mud, i.e. clay, shale and slate, but also with quartzsand and sandstone at greater depths the porosity declines (6). As a rule this phenomenon is called compaction. This has recently been treated at length by H. D. HEDBERG (2) and W. W. RUBEY (6).

The compaction of clay at no great depth is a consequence of this, that the adsorbed water at the points of contact of the solid particles is driven out enabling these particles to approach each other. The voids — under these circumstances pores can not be yet spoken of — then become smaller. If the pressure be again diminished, the clay then expands, so long as no other manner of compaction has taking place (3). During this first compaction the particles will also become arranged otherwise and owing to this, on the cessation of the pressure, even though it may be able to absorb water, the clay will not again expand to the volume it had before compaction set in.

The second way of compaction, the other arrangement of the solid particles is still able to proceed, even after the mutual contact has been attained, but then friction of the solid particles over each other takes place. That process, upon further compression, however, will cease when at all the points of contact of the solid particles the angle the direction of the pressure forms with the normal of the common tangent plane of two particles is smaller than a certain angle of friction. The gliding of the particles, however, can even then take place, provided the pressure increases in one direction and the above mentioned angles change, a proportional increase of the pressure in all directions, however, cannot any longer effect any compaction in this sense. It would even be conceivable that under alround pressure, as long as this manner of compaction is of effect, the volume of the clay or rock will become smaller without any increase of pressure. With the first kind of compaction however, by driving out the adsorbed water, a certain connection must exist between volume, respectively porosity and pressure (2).

If the pressure increases, compaction can take place in two other ways, viz : by recrystallization and by the crushing of the particles. With the recrystallization it may be presumed that at the points of contact of the particles, solid matter becomes dissolved and that this again becomes crystallised elsewhere on the surface of these particles. A new texture then arises ; this phenomenon was described by W. H. RUSSELL (5) for sandstone. The sediment then undergoes a change from a granular to spongy mass.

The crushing of some particles, as is discussed above, must again be succeeded by compaction, owing to alteration of the arrangements, by which the smaller particles occur, due to the crumbling of the larger, and force a way into the former pores.

If it be taken that the deposit of the sediments and the sinking of those already deposited takes place so slowly that compaction at any depth may be always considered as having been completed, as regards the pressure operating there, the porosity, at any depth, might be considered as a function of the pressure and the porosity would then indirectly be a function of the depth. From the foregoing observation, however, it would then follow that this need not be a continuous function. At a slight depth this function is determined by adsorption, and at greater dephts by entirely other phenomena.

The pressure exercised by a sediment of a certain porosity can be easily calculated as long as the mass is still granular. We then have to do with the pressure exercised by submerged bodies. If the specific gravity of the grains be s, and if the porosity (i.e. the quotient of the volume of the pores and that of the entire mass) p, then the weight of the solid matter in the unit of volume of the mass is $(1-p)\,s$, and the pressure of the water upwards upon this quantity of matter $1-p$, hence the pressure per unit of volume is $(1-p)\,(s-1)$. The specific gravity of the water is presumed to be 1.

Therefore at a depth y the pressure is :

$$D = (1-p)(s-1)\,y \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The hydrostatic pressure of a column of water of this height is y, hence the sediment exercises a pressure that is $(1-p)\,(s-1)$ times that of a column of water of the same height.

H. D. HEDBERG (2, p. 1038) states that according to C. K. LEITH and W. J. MEAD, the specific gravity of the solid particles of clay is 2.68, of shale 2.71 and 2.70—2.85 for slate. If 2.75 be taken as the average specific gravity :

$$(s-1)(1-p) = 1{,}75\,(1-p) \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

and for $p = 0.43$, the value of this form is 1. If the porosity of the sediment be 0.43, it then thus exercises a pressure, that is equally great as that of a column of water of the same height. If the porosity be smaller, the pressure becomes greater :

porosity	$(1-p)(s-1)$
0,4	1,05
0,3	1,22
0,2	1,40
0,1	1,57
0,01	1,73

The figures in the second column represent the pressure at the values of the porosity given in the first column, which a layer of granular sediment, having a thickness 1, exercises upon the grains of the sediment lying below there. This pressure multiplied by the depth, represents the pressure that aims at crushing, or bringing the grains closer together.

Formula (1) can also be deduced in another manner. If per unit of area at a depth y, the volume of the pores declines q, the whole mass of sediment with the water in its pores, with a thickness y, will sink a small depth q, on the other hand, however, a volume of water q will rise over a height y.

Hence the following energy is exerted :

1⁰. Positive, by the sediment : $(1-p)\ syq$.

2⁰. Positive, by the water : pyq.

3⁰. Negative, by the water : yq.

The total energy that is exerted by the sinking of the sediments is therefore :

$$A=\{(1-p)s+p-1\}yq=(1-p)(s-1)yq \quad . \; . \; . \; . \quad (3)$$

The distance is q, hence the force of the pressure exercised in this case, is

$$D=\frac{A}{q}=(1-p)(s-1)y, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

as deduced in formula (1).

The last deduction, that of formula (4) is unaltered of application for a porous rock, for a spongy mass, as is referred to above.

If the pressure will be able to result in the further compaction of the sediments, it must then exercise energy :

1⁰. to cause the solid particles to approach each other, to cause matter to recrystallise, to effect a plastic change of form, to crush particles and to cause particles to glide over each other ;

2⁰. To get the water to move from the diminished pore space through the pores of the sediments.

The work referred under 1⁰, may be spoken of as the compaction work, that referred to under 2⁰, is a loss, owing to friction in a fluid. The question would be whether that loss is great or small.

According to DARCY's law (see 4) the volume of water that flows per unit of time under a rate of decline $\frac{dh}{dl}$, the unit of area of the cross section in a sediment is:

$$u = k\frac{dh}{dl}, \qquad (5)$$

in which k is a factor dependent upon the nature of the sediment, if h is the pressure head and l the distance.

With an unvariable transversal section is:

$$u = k\frac{h}{l} \qquad (6)$$

or

$$h = \frac{ul}{k} \qquad (6a)$$

The energy exerted with this per unit of time is per unit of area:

$$a = uh = \frac{u^2 l}{k} \qquad (7)$$

If the sediments over the height y are homogeneous one can write:

$$a = \frac{u^2 y}{k} \qquad (8)$$

and

$$u = \frac{q}{t}, \qquad (9)$$

if t is the time in which the volume of pores, as is above discussed has decreased q. From this follows:

$$a = \frac{q^2 y}{kt^2} \qquad (10)$$

and the total energy per unit of area is:

$$A = at = \frac{q^2 y}{kt}. \qquad (11)$$

Hence the energy absorbed by the friction of the water is inversely proportional to the time of the compaction. This energy would effect a great counter pressure, provided A had a great value. If the compaction, however, takes place slowly, t becomes great and the value of A small, so that the friction can become so small as to be negligible.

The value of the factor k is very small for the finer sediments, for the larger it is much greater. If fine sediments become intermingled with some coarser strata, the water will then be carried off laterally by the last mentioned, and, owing to this, the friction becomes much smaller.

In formula (1), as has already been observed, the value of s changes slightly with the depth, but that of p is dependent upon the pressure and consequently also upon the depth, hence may be written:

$$p = f(y) \tag{12}$$

and the pressure through a thin layer of sediment having a thickness dy is thus for every depth:

$$D = \{1 - f(y)\}(s - 1)\, dy, \tag{13}$$

which follows from formula (1). Hence the total pressure at a depth y is:

$$D = (s - 1)\left\{ y - \int_0^y f(y)\, dy \right\} \tag{14}$$

As is mentioned above, for great values of y the function $f(y)$ is not continuous within the limits 0 and y, so the value of D will be better represented by:

$$D = (s - 1)\left\{ y - \int_0^{y_1} f_1(y)\, dy - \int_{y_1}^{y_2} f_2(y)\, dy \ldots - \int_{y_{n-1}}^{y_n} f_n(y)\, dy \right\}. \tag{15}$$

The functions $f_1, f_2, \ldots, f_n$ are not known otherwise than from observation, if this be possible. If the value of p at various depths be known, instead of formula (15) we may be able to be satisfied with:

$$D = (s - 1)(y - \Sigma\, p \triangle y), \tag{16}$$

in which $\triangle y$ are the various heights, concerning which the porosity is considered as having the certain value p. Hence $\Sigma \triangle y = y$.

H. D. HEDBERG (2, pp. 1052 and 1053) gives various figures for the porosity of clay, shale and slate, taken partially from H. C. SORBY (1). For slate these may decline to $\frac{1}{400}$.

To prevent misunderstanding it should further be pointed out that the pressure of the sediments which tries to cause those open spaces such as excavations at great depth, which are not entirely filled with water nor with air under great pressure, to collapse, must not be calculated in this manner. In this case at the deduction of formula (3) referred to sub. 3^0 the work qy does not intervene and in the place of formula (4) we may write:

$$\{(1 - p)s + p\}\, y \tag{17}$$

Hitherto it has been presumed that the specific gravity of the water is 1. If the water be salt, this is not so and thus the specific gravity of the water is s_1, the formula then becomes:

$$D = (1 - p)(s - s_1)\, y \tag{18}$$

Should the specific gravity of the water not be everywhere the same, in stead of s_1 a function of the depth y can be put.

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Mathematics. — *A One-Four Representation of a Complex of Twisted Cubics on the Points of Space.* By J. W. A. VAN KOL. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of October 29, 1927).

§ 1. The twisted cubics k^3 that pass through two given points H_1 and H_2, that have two given chords a_1 and a_2 and cut a given line a_3, may be represented on the points of space in the following way. We assume three lines a'_1, a'_2 and a'_3, and we suppose a projective correspondence to be established between the points of a_i and the planes of the pencil of planes with axis a'_i $(i=1, 2, 3)$. Let a curve k^3 cut a_1 in A_1 and A'_1, a_2 in A_2 and A'_2 and a_3 in A_3. Let us call the planes associated to these points resp. α_1 and α'_1, α_2 and α'_2 and α_3. To k^3 we shall now associate the four points $\alpha_1\alpha_2\alpha_3$, $\alpha'_1\alpha_2\alpha_3$, $\alpha_1\alpha'_2\alpha_3$ and $\alpha'_1\alpha'_2\alpha_3$. In this way any curve k^3 generally has four image points. Inversely in an arbitrary point P one curve k^3 is represented. For if A_1, A_2 and A_3 are the points of a_1, a_2 and a_3 that are associated resp. to the planes Pa'_1, Pa'_2 and Pa'_3 and if ω^2 is the quadratic surface that passes through H_1, H_2 and A_3 and contains a_1 and a_2, P is the image of that individual of the system of the twisted cubics on ω^2 that have a_1, hence also a_2, as chord, which is defined by the points H_1, H_2, A_1, A_2 and A_3.

§ 2. Between the pencils of planes with axes a'_2 and a'_3 there arises a projective correspondence by association to any plane through a'_2 of the plane through a'_3 that passes through the same point of a'_1. To this projective association there corresponds another, V_1, between the points of a_2 and those of a_3. Any of the ∞^2 twisted cubics k^3 that have the property that one of their points of intersection with a_2 and their point of intersection with a_3 correspond to each other on account of V_1, has two image points that coincide in one point of a'_1.

a'_1 and a'_2 are singular lines; in an arbitrary point P of a'_1 e.g. any of the ∞^1 curves k^3 that pass through the points of *a_2 and a_3 which are associated to the planes Pa'_2 and Pa'_3, has two coinciding image points.*

In the same way any of the ∞^2 curves k^3 that have the property that one of their points of intersection with a_1 and one of their points of intersection with a_2 are associated to each other on account of a certain projective correspondence V_3, has one image point in a point of a'_3.

a'_3 is a singular line; in any point P of a'_3 any of the ∞^1 curves k^3 passing through the points of a_1 and a_2 that are associated to the planes Pa'_1 and Pa'_2 has one image point.

The transversal t_{13} (resp. t_{23}) of a_1 and a_2 passing through H_1 (resp. H_2) is completed by the conics that pass through H_2 (resp. H_1) and cut a_1, a_2, a_3 and t_{13} (resp. t_{23}), to ∞^2 curves k^3 each of which has one image point on the intersection t'_{13} (resp. t'_{23}) of the planes that are associated to the points of intersection of t_{13} (resp. t_{23}) with a_1 and a_2.

There are two singular lines t'_{13} *and* t'_{23} *that cut* a'_1 *and* a'_2*; an arbitrary point* P *of* t'_{13} *e.g. is one image point of each of the* ∞^1 *curves* k^3 *formed by* t_{13} *and the conics that pass through* H_2 *and the point of* a_3 *associated to the plane* Pa'_3 *and that lie on the quadratic surface defined by these two points and the three lines* a_1, a_2 *and* t_{13}.

The transversal t_{12} of a_1 and a_3 through H_1 is completed by the conics that lie in the plane $H_2 a_2$, pass through H_2 and cut a_1 and t_{12}, to ∞^2 curves k^3 each of which has two image points on the intersection t'_{12} of the planes that are associated to the points of intersection of t_{12} with a_1 and a_3 and two image points on the intersection t''_{12} of the planes that are associated to the point of intersection of t_{12} with a_3 and the point of intersection of the plane $H_2 a_2$ with a_1.

There are four singular lines t'_{12}, t''_{12}, t'_{22}, t''_{22} *that cut* a'_1 *and* a'_3 *and four singular lines* t'_{11}, t''_{11}, t'_{21}, t''_{21} *that cut* a'_2 *and* a'_3*; e.g. any point* P *of* t'_{12}, *hence also a point of* t''_{12}, *is one image point of each of the* ∞^1 *curves* k^3 *formed by* t_{12} *and the pencil of conics lying in the plane* $H_2 a_2$, *passing through* H_2 *and the point of* a_2 *that corresponds to the plane* Pa'_2, *and cutting* a_1 *and* t_{12}.

The conics that lie in the plane $H_1 a_2$, pass through H_1 and cut a_1 and a_3, are completed by the lines passing through H_2 and cutting them and a_1 in different points, to ∞^2 curves k^3 each of which has two image points on the intersection s_{12} of the planes that are associated to the points of intersection of a_1 and a_3 with the plane $H_1 a_2$.

There are two more singular lines s_{12} *and* s_{22} *that cut* a'_1 *and* a'_3 *and two singular lines* s_{11} *and* s_{21} *that cut* a'_2 *and* a'_3*; any point* P *of* s_{12} *e.g. is one image point of each of the* ∞^1 *curves* k^3 *formed by the pencil of conics that lie in the plane* $H_1 a_2$, *pass through* H_1 *and the point of* a_2 *corresponding to the plane* Pa'_2, *and cut* a_1 *and* a_3, *and the lines passing through* H_2 *and cutting* a_1 *and an individual of this pencil in different points.*

The planes that pass through H_1 and H_2 define three projective point ranges on a_1, a_2 and a_3. To them there correspond three projective pencils of planes with axes a'_1, a'_2 and a'_3, that produce a twisted cubic k^3_1 which has a'_1, a'_2 and a'_3 as chords. In the same way to the three projective point ranges defined on these lines by the transversals of a_1, a_2 and a_3, there correspond three projective pencils of planes with the axes a'_1, a'_2 and a'_3 that produce a twisted cubic k^3_2 which has likewise a'_1, a'_2 and a'_3 as chords. From the above it follows that the conics passing through H_1 and H_2 and cutting a_1, a_2 and a_3 are completed by the transversals of a_1 and a_2 cutting them, to ∞^2 curves k^3 each of which has one image point on k_1^3; and that the transversals of a_1, a_2 and a_3, are completed by the conics that pass through H_1 and H_2 and cut a_1, a_2 and one of these transversals, to ∞^2 curves k^3 each of which has one image point on k_2^3.

There are two singular twisted cubics k_1^3 and k_2^3 that have a_1', a_2' and a_3' as chords; any point of k_1^3 is one image point of each of the ∞^1 curves k^3 formed by a certain conic that passes through H_1 and H_2 and cuts a_1, a_2 and a_3, and the transversals of a_1, a_2 and the said conic, which transversals form a scroll lying on the quadratic surface that is defined by a_1, a_2 and the conic in question; any point of k_2^3 is one image point of each of the ∞^1 curves k^3 formed by a certain transversal of a_1, a_2 and a_3 and the conics that pass through H_1 and H_2 and lie on the quadratic surface defined by H_1, H_2, a_1, a_2 and the said transversal; k_1^3 cuts the lines t_{ik}' $(i=1, 2;\ k=1, 2, 3)$ and k_2^3 the lines s_{ik} $(i, k=1, 2)$.

§ 3. The transversals of a_1', a_2' and a_3' define three projective pencils of planes with axes a_1', a_2' and a_3'. To them there correspond three projective point ranges on a_1, a_2 and a_3. Each of the ∞^1 curves k^3 that have the property that one of their points of intersection with a_1, one of their points of intersection with a_2 and their point of intersection with a_3 are associated points of the said projective point ranges on a_1, a_2 and a_3, is a singular curve of our complex; for it has all points of a certain transversal of a_1', a_2' and a_3' as image points (besides it has three more image points lying in the plane that is defined by this transversal and a_3'). We have to prove that the singular curves k^3 form a surface of the fourteenth degree which has sevenfold points in H_1 and H_2, and that a_1, a_2 and a_3 are single lines of the surface.

§ 4. The system Σ_1 of the curves k^3 that pass through a given point P, lies on the quadratic surface ω^2 which passes through H_1, H_2 and P and contains a_1 and a_2. If we call the points of intersection of a_3 with ω^2 S_1 and S_2, we can decompose Σ_1 into the systems Σ_1' and Σ_1'' formed by the curves of Σ_1 that pass through S_1 resp. S_2. The image curves k_p' and k_p'' of Σ_1' and Σ_1'' lie in the planes $\varkappa'$ and $\varkappa''$ through a_3' that are associated to S_1 resp. S_2. The curves of Σ_1' as well as those of Σ_1'' produce a (2, 2)-correspondence between the points of a_1 and those of a_2. To them correspond (2, 2)-correspondences, between the planes through a_1' and those through a_2'. Consequently k_p' en k_p'' are biquadratic plane curves that have nodes in the points of intersection of a_1' and a_2' with $\varkappa'$ resp. $\varkappa''$.

k_p' and k_p'' cut each of the lines t_{13}' and t_{23}' in one point; the point of intersection of k_p' and t_{13}' e.g, is the image of the curve k^3 formed by t_{13} and the conic on ω^2 that passes through H_2, P and S_1.

k_p' and k_p'' cut each of the curves k_1^3 and k_2^3 in one point; the point of intersection of k'_p and k_1^3 is an image of the curve k^3 formed by the conic on ω^2 that passes through H_1, H_2 and S_1 and the transversal through P of a_1 and a_2 and the point of intersection of k'_p and k_2^3 is an image of the curve k^3 formed by the conic on ω^2 that passes through H_1, H_2 and P and the transversal through S_1 of a_1 and a_2. Summarizing:

The system of the curves k^3 that pass through a given point P, is represented on two biquadratic plane curves k'_p and k''_p of which the planes pass through a'_3, which have both a node on a'_1 as well as on a'_2 and both of which cut the lines t'_{13} and t'_{23} and the curves k_1^3 and k_2^3 in one point.

§ 5. Let us call O_l the image surface of the system Σ_2 of the curves k^3 that cut a given line l. We determine the degree of O_l by cutting it by a transversal t of a'_1 and a'_2. The number of points of intersection outside a'_1 and a'_2 is equal to the number of curves k^3 of Σ_2 that pass through a point A_1 of a_1 and a point A_2 of a_2. Now the twisted cubics that pass through H_1, H_2, A_1 and A_2, cut a_3 and l and also cut a_1 outside A_1, form a surface of the thirteenth degree that has a seven-fold point in A_2[1]). Accordingly the number of curves of Σ_2 that pass through A_1 and A_2, hence the number of points of intersection of t and O_l outside a'_1 and a'_2, is equal to six. Further a'_1 and a'_2 are quadruple lines of O_l, what appears as follows. The multiplicity of a'_1 is equal to twice the number of curves of Σ_2 that pass through a point A_2 of a_2 and a point A_3 of a_3. Now the twisted cubics that pass through H_1, H_2, A_2 and A_3, have a_1 as chord and cut l, form a biquadratic surface that has double points in H_1, H_2, A_2 and A_3 [2]) and, accordingly, is cut by a_2 in two points outside A_2. From this there follows at once the indicated multiplicity of a'_1 and a'_2. Accordingly the line t cuts O_l in all in fourteen points so that we have proved that O_l is of the degree fourteen.

a'_3 is a sextuple line of O_l. For the multiplicity of a'_3 is equal to the number of curves of Σ_2 that pass through a point A_2 of a_2 and a point A_1 of a_1, hence, as we have shown above, equal to six.

We shall give the other properties of O_l without proof.

The system of the curves k^3 that cut a given line l, is represented on a surface O_l of the fourteenth degree that has a'_1 and a'_2 as quadruple lines, a'_3 as a sextuple line, the lines t'_{ik} and t''_{ik} as single lines, the lines t'_{13}, t'_{23} and s_{ik} $(i, k = 1, 2)$ as double lines and k_1^3 and k_2^3 as double curves.

For the intersection of the curves k'_p and k''_p with O_l we find besides singular lines and curves sixteen points of intersection, whence there ensues the following property, which may be proved directly in a simpler way:

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[1]) Cf. G. SCHAAKE, The Congruence of the Twisted Cubics which Pass through Four Given Points and Cut Two Given straight Lines. These Proceedings, 29, p. 1020.

[2]) Cf. G. SCHAAKE, A Representation of the Congruence of the Twisted Cubics which pass through Four Given Points and cut a Given straight Line Twice. These Proceedings **29**, p. 776.

There are four twisted cubics that pass through three given points, have two given chords and cut two given lines.

§ 6. The intersection of O_l and O_m consists of singular lines and curves, eventually to be counted more than once, and a curve k_{lm} of the order 72. Evidently k_{lm} is the image curve of the system Σ_3 of the curves k^3 that cut two given lines l and m.

k_{lm} cuts a_3' in 56 points. For the number of points of intersection outside a_3' of k_{lm} and a plane through a_3' is equal to four times the number of curves k^3 that pass through a point of a_3 and cut l and m. Accordingly k_{lm} cuts a_3' in $72 - 4.4 = 56$ points.

The number of points of intersection of k_{lm} and a_1' is equal to twice the number of curves of Σ_3 with the property that their point of intersection with a_3 and one of their points of intersection with a_2 are associated to each other through the projective correspondence V_1. In order to determine this number we associate to an arbitrary point A_3 of a_3 the eight points A_3' that on account of V_1 are associated to the points where a_2 is cut by the four curves of Σ_3 through A_3. If for the moment we call x the number of curves of Σ_3 that pass through a point of a_2, inversely to a point A_3' there correspond x points A_3. As the $(x, 8)$-correspondence between the points A_3 en A_3' has $x+8$ coincidences, k_{lm} cuts a_1' in $2x+16$ points. We arrive at the number x by determining in another way the number of points of intersection of k_{lm} and a_3', which has already been found above. For this number is also equal to the number of curves of Σ_3 with the property that one of their points of intersection with a_1 and one of their points of intersection with a_2 correspond to each other on account of the projective correspondence V_3. If now to an arbitrary point A_1 of a_1 we associate the $2x$ points A_1' that through V_3 correspond to the points where a_2 is cut by the x curves of Σ_3 through A_1, inversely to an arbitrary point A_1' there correspond $2x$ points A_1. The $(2x, 2x)$-correspondence between the points A_1 and A_1' found in this way, has $4x$ coincidences. As above we have already found 56 for this number, we know now that $x = 14$.

Consequently k_{lm} cuts each of the lines a_1' and a_2' in 44 points.

k_{lm} cuts each of the lines t_{13}' and t_{23}' in ten points. t_{13} e.g. is completed by each of the conics that pass through H_2 and cut a_1, a_2, a_3, l, m and t_{13} (outside the points of intersection of t_{13} with a_1 and a_2) to a curve k^3 that has an image point in a point of intersection of k_{lm} and t_{13}'. The number of these conics is ten, because the conics through H_2 that cut a_1, a_2, a_3, l and m, form a surface of the eighteenth degree that has a_1, a_2, a_3, l and m as quadruple lines and, accordingly, is cut by t_{13} in ten more points outside a_1 and a_2. [1])

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[1]) Cf. SCHUBERT, Kalkül der abzählenden Geometrie, p. 96, where the numbers $P\nu^6 = 18$ and $P^2\nu^4 = 4$ have been deduced.

k_{lm} cuts each of the lines t'_{ik} and t''_{ik} $(i, k = 1, 2)$ in two points and each of the lines s_{ik} $(i, k = 1, 2)$ in six points.

k_{lm} cuts k_1^3 in twenty points. This appears in the following way. The conics through H_1 and H_2 that cut a_1, a_2 and a_3, form a biquadratic surface of which a_1, a_2 and a_3 are single lines. Hence there are four conics that pass through H_1 and H_2 and cut a_1, a_2, a_3 and l. Each of these conics is completed by the two lines that cut it and a_1, a_2 and m in different points, to two curves k^3 that have an image point in one point of intersection of k_{lm} and k_1^3. Thus we have found four nodes of k_{lm} on k_1^3. We find four more of such points by interchanging l and m. Finally each of the two transversals of a_1, a_2, l and m is completed by the two conics through H_1 and H_2 that cut it and a_1, a_2 and a_3 in different points, to two curves k^3 each of which has an image point in a point of intersection of k_{lm} and k_1^3. In this way we have found four more, hence in all twenty, points of intersection of k_{lm} and k_1^3.

In an analogous way we can show that k_{lm} and k_2^3 cut each other in sixteen points.

The system of the curves k^3 that cut two given lines l and m, is represented on a curve k_{lm} of the order 72 that is cut by a'_1 and a'_2 in 44 points, by a'_3 in 56 points, by each of the lines t'_{13} and t'_{23} in 10 points, by each of the lines t'_{ik} and t''_{ik} $(i, k = 1, 2)$ in 2 points, by each of the lines s_{ik} in 6 points, by k_1^3 in 20 points and by k_2^3 in 16 points.

k_{lm} cuts O_n in 144 points outside singular lines and curves. Hence:

There are 36 twisted cubics that pass through two given points, have two given chords and cut four given lines.

§ 7. We can also investigate the representations of different systems of curves k^3, e.g. the systems of the curves k^3 that cut a_3 twice, that have a given chord, that touch a given plane, that touch two given planes and others.

The numbers that may be deduced from the representations of the said systems and the numbers already deduced above, are the following:

$$\begin{array}{lll}
P^3 B^3 = 1 & P^2 B^4 = 1 & P^2 B^2 \nu^4 = 36 \\
P^3 B^2 \nu^2 = 4 & P^2 B^3 \nu^2 = 6 & P^2 B^2 \nu^3 \varrho = 72 \\
P^3 B^2 \nu \varrho = 8 & P^2 B^3 \nu \varrho = 12 & P^2 B^2 \nu^2 \varrho^2 = 144 \\
 & P^2 B^3 \varrho^2 = 24 & P^2 B^2 \nu \varrho^3 = 288
\end{array}$$

Here P denotes the condition that a twisted cubic pass through a point, B that it have a given chord, ν that it cut a given line and ϱ that it touch a given plane.

§ 8. The above enables us to indicate properties of surfaces formed by systems of ∞^1 curves k^3.

The curves k^3 that have a given chord b, form a surface of the sixth degree with triple points in H_1 and H_2; a_1, a_2 and b are double lines and a_3 is a single line of this surface.

The curves k^3 that cut two given lines l and m, form a surface of the degree 36 that has eighteen-fold points in H_1 and H_2; a_1 and a_2 are fourteen-fold lines, a_3, l and m are quadruple lines, and the transversals of a_1 and a_2 through H_1 and H_2 are ten-fold lines of this surface. Etc.

§ 9. These results may be generalised by replacing the given chords a_1 and a_2 and the given line a_3 by rational twisted curves. We must then make use of a few numbers relating to the congruences of the twisted cubics that pass through four given points and besides either cut a given rational twisted curve twice or cut two given rational twisted curves. With a view to this I refer to the thesis for the doctorate of the author: "Over congruenties en complexen van kubische ruimtekrommen".

Physics. — *The ice-point of the Thermometer scale.* (19th communication of results obtained by the aid of the "VAN DER WAALS Fund".) By A. MICHELS and F. COETERIER. (Preliminary communication.) (Communicated by Prof. J. D. VAN DER WAALS.)

(Communicated at the meeting of November 26, 1927).

A difficulty arising in connection with the determination of isotherms, was the impossibility of determining the 0° (Celsius) point of the thermometer scale with sufficient reproducibility by means of the methods in ordinary use. A greater constancy than 1/100, corresponding at 0° to a temperature accuracy of 1/27300, could not be obtained with certainty, whilst the volume and pressure measurements were susceptible to a much higher reproducibility. The cause of the inconstancy of the ice point has been traced, and a search made for a further point to serve better as the fixed point of the temperature scale.

One of the chief causes of the irregularity is that the ice point is never in a truly unary system, for even if ice from very pure distilled water is available, dissolved gases would still remain as impurities.

A block of commercial ice usually consists of a transparent mass surrounding an opaque core and this core has much the higher gas content.

Nitrogen and Oxygen are the most likely gases to be present, and the saturation of water by these gases at atmospheric pressure results in the freezing point being lowered by 2.5×10^{-3}. Other gases which are always present in a laboratory atmosphere will also be dissolved. Every mm. of Carbon dioxide, for example, will, when the dissociation of dissolved H_2CO_3 is considered, result in a depression of the freezing point of 0.6×10^{-3}.

The products of the combustion of coal gas will also add to the impurities of the atmosphere and, therefore, of the water from the melting ice.

The handling of ice during crushing and contact with a machine may also lead to the picking up of slight impurities.

The constancy given by the triple point of water has therefore been investigated, as all these difficulties may then be avoided and a clearly defined unary system adopted.

Preliminary determinations.

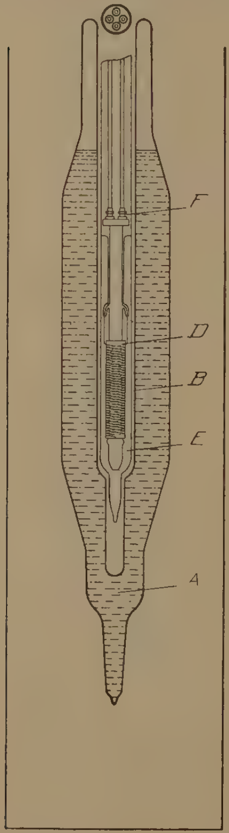
In order to see whether the use of the triple point was practicable, a glass vessel was made in the form of a Dewar-vessel, and the space between the two walls filled with distilled and gas-free water.

The water in the space was supercooled and then crystallised by touching the outside wall with a piece of solid carbon dioxide.

This method of supercooling appeared to possess a great advantage over direct crystallisation. The water was supercooled at every point and, during the crystallisation, the ice needles shot from all sides simultaneously towards the inside of the vessel.

A quantity of mercury was poured into the inner vessel in order to obtain a better temperature exchange, and the bulb of a BECKMANN thermometer was placed in the mercury.

The first experiments gave a temperature variation of only 1/500°. Some of the needles showed that the ice began to melt soon after crystallisation, and the temperature did not remain constant for more than ten minutes.



Further observations.

As the results obtained were favourable, an improved and more definite apparatus was constructed.

A much larger vessel was made, again in the form of a Dewar glass, as shown in the figure (capacity about 1 litre). The space *A* contained gas-free distilled water, and *B* mercury.

The vessel was made large enough to hold a BECKMANN thermometer with the whole length of the Hg thread in the vessel.

The vessel was supercooled by about 4° and, after the water had been crystallised as before, surrounded by a jacket (*C*) containing crushed ice.

As the temperature between C and *A* only differed by 1/100°, the heat exchange between *A* and its surroundings was reduced to a minimum.

It was possible by this means to maintain the temperature in *B* constant for several hours.

Observations with the BECKMANN thermometer divided in hundredths of a degree, and therefore readable to a thousandth, showed no observable variations during the course of one crystallisation and, when the experiment was repeated on different days, the same result was obtained within the accuracy of observation.

Although this accuracy was more than enough for the immediate researches, it appeared advisable to investigate how far the accuracy extended by another method and observations were therefore made with a platinum thermometer.

The platinum thermometer, which was specially made for the purpose, consisted of a platinum wire loosely wound on a porcelain tube *D*, contained in a sealed glass vessel *E*, filled with distilled paraffin (Boiling point 210°).

In order to reduce thermal currents, the points *F*, where the platinum was connected to copper wire, were made so that they were in the constant temperature zone.

The insulation resistance of the platinum thermometer was greater than 10^9 Ohms, and the lag to 1/4000° was two minutes.

The resistance of the platinum thermometer was measured with a potentiometer, and was about 16.3 Ohms at 0°.

The sensitivity of the electrical circuit was so adjusted that a variation of $1.5 \times 10^{-5}\ \Omega$ gave a deflection of the galvanometer of 0.1 mm on the scale.

A greater accuracy of the electrical measurements could not be obtained.

A series of readings, taken on different days, gave a resistance of

16.28838
39
36
36

The vessel was then opened and refilled with fresh gas-free distilled water.

Two different readings gave 16.28839
38

giving a total mean of $16.28837 \pm 1^5 \times 10^{-5}$,
which is exactly the maximum reproducibility of the electrical measurements, and which corresponds to a constancy of the temperature of within 2.3×10^{-4}°.

The two samples of water used were distilled three times. A good criterion of the purity of the water could be obtained during the measurements from the ease with which the water could be supercooled.

Both the samples of water used remained supercooled despite the reversing of the vessel and the rather violent movement during the removal of the freezing mixture.

The influence of the solubility of silicates from the glass walls on the freezing point still remains to be investigated.

No precautions were taken to choose a special glass, and ordinary laboratory glass was used, the vessel being well steamed out before filling.

The solid residues from the two samples of water used were determined, and the authors are indebted to Prof. J. B. WIBAUT for his kindness in allowing these determinations to be made in his laboratory.

The first sample gave a dry residue of 12.5 and the second of 8.4 milligrams per litre. As the form in which these silicates were present was unknown, it is not possible to say how far the lowering of the freezing point will be influenced, but, in the most unfavourable case, the lowering of the triple point must be much less than 1/1000°.

Although the water used had remained sealed in glass for one year, it thus appears that the influence of dissolved silica is small.

It will be necessary to repeat the determination with other kinds of glass that have a special resistance to the etching action of water, and with a platinum thermometer of still greater sensitivity.

The influence of the degree of super-cooling on the readings of the thermometer must also be investigated.

An indication that such an influence may exist arose from the fact that a third filling, in which the super cooling did not once go smoothly, gave a temperature difference of 1/1500 degrees. It is not impossible that this result was influenced by a slight impurity.

As a result of the above, it appears desirable to make the triple point of water the fixed point of the temperature scale in place of the icepoint.

In order to obtain an easier connection with the existing scale, it is suggested that *the 0° Celsius point be defined as that point lying 0.007° lower than the triple point of water.*

From the course of the melting point curve of H_2O, this will then be the temperature difference between the freezing and triple points.

Mathematics. — *Linear Adjustment of a Set of Pairs of Numbers* (x_k, y_k). By Prof. M. J. VAN UVEN. (Communicated by Prof. A. A. NIJLAND).

(Communicated at the meeting of November 26, 1927).

If, by some theoretical consideration, we assume a linear relation $\alpha x+\beta y+\gamma=0$ between two variables x and y, the experiment however furnishing a set of n pairs $(x_1, y_1), (x_2, y_2), \ldots (x_n, y_n)$ not agreeing completely with the same linear relation, the values x_k, y_k $(k=1, \ldots n)$ obtained by experiment, and therefore subject to errors of observation, must be adjusted.

We have in general no right to consider one of the variables as free from error. So both values x_k and y_k must be "corrected".

Speaking geometrically we have the problem: To fit a straight line L as closely as possible through n points S_k having coordinates x_k, y_k $(k=1, \ldots n)$ given by experiment.

As a rule no straight line exists, which passes exactly through all the given points S_k. Calling T_k for convenience sake the true position of S_k, the displacement $\delta_k=\overrightarrow{S_k T_k}$ is the correction of S_k, and $\overrightarrow{T_k S_k}=-\delta_k$ is the "error" of S_k. Generally both x_k and y_k must be corrected; that is to say: the displacements δ_k will not in general coincide with the direction of any coordinate.

We must also take into account the possibility that the x-coordinate has an uncertainty (mean error, weight) different from that of the y-coordinate. Nor is a certain dependence between the error $\triangle x$ of x and the error $\triangle y$ of y to be excluded; this dependence is revealed by the fact that the mean value of $\triangle x_k \,.\, \triangle y_k$ differs from zero.

We may consider the xy-plane as subject to elastic tensions, which perform a certain (negative) work by the displacement of a point, whence a certain potential energy is produced.

The plane not being isotropic, the elastic tension has its maximum and its minimum in two directions, perpendicular to each other, which need not coincide with the directions of the coordinate-axes.

We shall treat the given problem on the most general supposition: viz. that the plane is not isotropic, and that the main directions of elasticity form an angle (ω) with the coordinate-axes.

Each point S_k being shifted by a displacement δ_k to a point T_k, situated on a certain straight line L, there will be produced a certain total amount V of potential energy.

As the line L, best fitted through the points S_k, we shall consider that line L_0 for which the total potential energy V takes its minimum value.

The angle between the axes of elasticity and the coordinate-axes being ω, the coordinates x', y' of a point with respect to a system of coordinates having the same origin as the system x, y, and parallel to the axes of elasticity, are connected with x and y by

$$x' = x \cos \omega + y \sin \omega,$$
$$y' = -x \sin \omega + y \cos \omega.$$

The modulus of elasticity (elastic force in displacing a point over the distance 1) in the main direction x' being P, in the main direction y' Q, a displacement in the direction which makes the angle ζ' with the positive axis of x', generates an elastic force $\mathfrak{E}$ the components of which are

$$E_{x'} = -P \cos \zeta' \quad , \quad E_{y'} = -Q \sin \zeta' \quad . \quad . \quad . \quad . \quad (1)$$

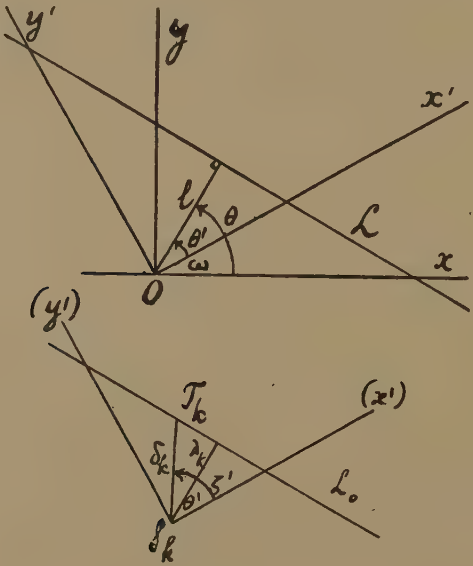


Fig. 1.

This force is balanced by the force attracting the point perpendicularly to L. This latter force having the components $+P \cos \zeta'$, $+Q \sin \zeta'$, the direction θ' of the normal of L is connected with the direction ζ' by the relation

$$\frac{E_{y'}}{E_{x'}} = \operatorname{tg} \theta' = \frac{Q \sin \zeta'}{P \cos \zeta'},$$

or

$$\frac{\sin\zeta'}{\cos\zeta'} = \frac{P\sin\theta'}{Q\cos\theta'},$$

thus

$$\cos\zeta' = \frac{Q\cos\theta'}{\sqrt{P^2\sin^2\theta' + Q^2\cos^2\theta'}}, \quad \sin\zeta' = \frac{P\sin\theta'}{\sqrt{P^2\sin^2\theta' + Q^2\cos^2\theta'}}. \quad (2)$$

The angle $\zeta' - \theta'$ between the directions of displacement and force is determined by

$$\cos(\zeta' - \theta') = \frac{Q\cos^2\theta' + P\sin^2\theta'}{\sqrt{P^2\sin^2\theta' + Q^2\cos^2\theta'}}. \quad . \quad . \quad . \quad . \quad (3)$$

So the component of the elastic force in displacing the point over the distance 1 in the direction ζ' (i.e. in the direction from S_k to T_k) amounts to

$$E_{\zeta'} = E_{x'}\cos\zeta' + E_{y'}\sin\zeta' = -(P\cos^2\zeta' + Q\sin^2\zeta') = -\frac{PQ^2\cos^2\theta' + QP^2\sin^2\theta'}{P^2\sin^2\theta' + Q^2\cos^2\theta'},$$

or

$$E_{\zeta'} = -PQ\,.\,\frac{P\sin^2\theta' + Q\cos^2\theta'}{P^2\sin^2\theta' + Q^2\cos^2\theta'}. \quad . \quad . \quad . \quad . \quad (4)$$

Hence the displacement δ_k (in the direction ζ') generates a force, the component of which in the direction ζ' (i. e. in the direction from S_k to T_k) is

$$E_{\zeta'}\,.\,\delta_k\,.$$

By displacing S_k gradually to T_k on L, this component performs the work:

$$\int_0^{\delta_k} E_{\zeta'}\,.\,\delta\,.\,d\delta = \tfrac{1}{2}\,E_{\zeta'}\,.\,\delta_k^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The perpendicular distance λ_k from S_k to L being

$$\lambda_k = \delta_k\cos(\zeta' - \theta'),$$

we have

$$\delta_k = \frac{\lambda_k}{\cos(\zeta' - \theta')} = \lambda_k\,.\,\frac{\sqrt{P^2\sin^2\theta' + Q^2\cos^2\theta'}}{P\sin^2\theta' + Q\cos^2\theta'} \quad . \quad . \quad . \quad (6)$$

From (4) and (6) follows that the work performed (5) amounts to

$$\tfrac{1}{2}\,E_{\zeta'},\,\delta_k^2 = -\frac{PQ}{2}\,.\,\frac{P\sin^2\theta' + Q\cos^2\theta'}{P^2\sin^2\theta' + Q^2\cos^2\theta'} \times \frac{P^2\sin^2\theta' + Q^2\cos^2\theta'}{(P\sin^2\theta' + Q\cos^2\theta')^2} \times \lambda_k^2$$

$$= -\frac{PQ}{2}\,.\,\frac{\lambda_k^2}{P\sin^2\theta' + Q\cos^2\theta'}.$$

Denoting by [ ] the summation over k from 1 to n, we find for all the points S_k together:

$$\tfrac{1}{2} E_{\zeta'} . [\delta_k^2] = -\frac{PQ}{2} \frac{[\lambda_k^2]}{P \sin^2 \theta' + Q \cos^2 \theta'} \quad . \quad . \quad . \quad . \quad (7)$$

So the potential energy produced is

$$V = -\tfrac{1}{2} E_{\zeta'} . [\delta_k^2] = +\frac{PQ}{2} \cdot \frac{[\lambda_k^2]}{P \sin^2 \theta' + Q \cos^2 \theta''} \quad . \quad . \quad . \quad (8)$$

or, denoting the mean value $\dfrac{[\lambda_k^2]}{n}$ of λ_k^2 by $\overline{\lambda_k^2}$,

$$V = \frac{nPQ}{2} \cdot \frac{\overline{\lambda_k^2}}{P \sin^2 \theta' + Q \cos^2 \theta'} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Introducing the perpendicular distance l from O to L, we find:

$$\lambda_k = x'_k \cos \theta' + y'_k \sin \theta' - l,$$

therefore

$$V = \frac{nPQ}{2} \cdot \frac{\overline{(x'_k \cos \theta' + y'_k \sin \theta' - l)^2}}{P \sin^2 \theta' + Q \cos^2 \theta'} \cdot \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Passing to the original system of coordinates x, y, we have

$$\theta' = \theta - \omega,$$

$$x'_k \cos \theta' + y'_k \sin \theta' = x_k \cos \theta + y_k \sin \theta,$$

$$\begin{aligned} P \sin^2 \theta' + Q \cos^2 \theta' &= P \sin^2 (\theta - \omega) + Q \cos^2 (\theta - \omega) \\ &= (P \sin^2 \omega + Q \cos^2 \omega) \cos^2 \theta + \\ &\qquad + 2 (-P + Q) \sin \omega \cos \omega \cos \theta \sin \theta + \\ &\qquad + (P \cos^2 \omega + Q \sin^2 \omega) \sin^2 \theta. \end{aligned}$$

Putting

$$\left. \begin{aligned} a &= P \sin^2 \omega + Q \cos^2 \omega, \\ b &= (-P + Q) \sin \omega \cos \omega, \\ c &= P \cos^2 \omega + Q \sin^2 \omega, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we find:

$$P \sin^2 \theta' + Q \cos^2 \theta' = a \cos^2 \theta + 2\, b \cos \theta \sin \theta + c \sin^2 \theta = f(\theta). \quad (12)$$

Hence the potential energy V is

$$V = \frac{nPQ}{2} \times \frac{\overline{\lambda_k^2}}{f(\theta)} = \frac{nPQ}{2} \times \frac{\overline{(x_k \cos \theta + y_k \sin \theta - l)^2}}{a \cos^2 \theta + 2\, b \cos \theta \sin \theta + c \sin^2 \theta} \quad (13)$$

The forces are in balance if V is a minimum, thus if

$$\frac{2V}{nPQ} = \varphi(\theta, l) = \frac{\overline{\lambda_k^2}}{f(\theta)} = \frac{\overline{(x_k \cos \theta + y_k \sin \theta - l)^2}}{a \cos^2 \theta + 2\, b \cos \theta \sin \theta + c \sin^2 \theta} \text{ minimum.} \quad (14)$$

Putting

$$\bar{x} = \frac{[x_k]}{n}, \quad \bar{y} = \frac{[y_k]}{n},$$

and

$$x_k = \bar{x} + u_k\,, \quad y_k = \bar{y} + v_k\,,$$

whence

$$\bar{u} = 0, \bar{v} = 0,$$

we find:

$$\overline{(x_k \cos\theta + y_k \sin\theta - l)^2} = \overline{\{(\bar{x}\cos\theta + \bar{y}\sin\theta - l) + (u_k \cos\theta + v_k \sin\theta)\}^2}$$
$$= (\bar{x}\cos\theta + \bar{y}\sin\theta - l)^2 + 2\,(\bar{x}\cos\theta + \bar{y}\sin\theta - l)(\bar{u}\cos\theta + \bar{v}\sin\theta) +$$
$$+ (\overline{uu}\cos^2\theta + 2\,\overline{uv}\cos\theta\sin\theta + \overline{vv}\sin^2\theta).$$

Taking into account $\bar{u} = 0$, $\bar{v} = 0$, and putting:

$$\overline{uu} = A,\ \overline{uv} = B,\ \overline{vv} = C, \quad \ldots\ldots\ldots \quad (15)$$

we arrive at

$$\left.\begin{array}{l}\overline{(x_k \cos\theta + y_k \sin\theta - l)^2} = (\bar{x}\cos\theta + \bar{y}\sin\theta - l)^2 + \\ \qquad\qquad + (A\cos^2\theta + 2\,B\cos\theta\sin\theta + C\sin^2\theta).\end{array}\right\} \quad (16)$$

So the condition (14) runs:

$$\varphi(\theta,l) = \frac{(\bar{x}\cos\theta + \bar{y}\sin\theta - l)^2 + (A\cos^2\theta + 2B\cos\theta\sin\theta + C\sin^2\theta)}{a\cos^2\theta + 2\,b\cos\theta\sin\theta + c\sin^2\theta}\ \text{minimum} \quad (17)$$

The condition of minimum $\frac{\partial\varphi}{\partial l} = 0$ furnishes

$$\frac{\partial\varphi}{\partial l} = \frac{-2\,(\bar{x}\cos\theta + \bar{y}\sin\theta - l)}{f(\theta)} = 0,$$

or

$$\bar{x}\cos\theta + \bar{y}\sin\theta - l = 0; \quad \ldots\ldots\ldots \quad (18)$$

that is to say: the line L required must pass through the "mean point" $(\bar{x}, \bar{y})$.

Th condition (17) asks now

$$\varphi(\theta) = \frac{A\cos^2\theta + 2\,B\cos\theta\sin\theta + C\sin^2\theta}{a\cos^2\theta + 2\,b\cos\theta\sin\theta + c\sin^2\theta}\ \text{minimum}, \ . \quad (19)$$

or, putting

$$A\cos^2\theta + 2B\cos\theta\sin\theta + C\sin^2\theta = F(\theta), \quad \ldots \quad (20)$$

$$\varphi(\theta) = \frac{F(\theta)}{f(\theta)}\ \ \text{minimum} \ \ldots\ldots\ldots \quad (19')$$

From (19) (or (19′)) we take the value of θ which minimizes $\varphi(\theta)$; denoting this solution by θ_0, and the value of l required, by l_0, we have, on account of (18),

$$l_0 = \bar{x}\cos\theta_0 + \bar{y}\sin\theta_0 \quad \ldots\ldots\ldots \quad (21)$$

From

$$A = \overline{uu} = \frac{[u_k^2]}{n}\ , \quad B = \overline{uv} = \frac{[u_k v_k]}{n}\ , \quad C = \overline{vv} = \frac{[v_k^2]}{n}$$

follows

$$A > 0 \quad \text{and} \quad AC - B^2 = \frac{[u_k^2]\,[v_k^2] - [u_k\, v_k]^2}{n^2} = \frac{[(u_k\, v_l - u_l\, v_k)^2]}{n^2} > 0.$$

Likewise, from (11) ensues:

$$a > 0 \quad \text{and} \quad ac - b^2 = PQ > 0.$$

So both the forms $F(\theta)$ and $f(\theta)$ are positive definite.

Hence the present minimumproblem: $\dfrac{F(\theta)}{f(\theta)}$ min. is formally equivalent to determining the direction of minimum curvature at an elliptic point of a surface.

Putting:

$$\left.\begin{aligned} \operatorname{tg} \theta &= z, \\ A + 2\,Bz + Cz^2 &= G(z), \\ a + 2\,bz + cz^2 &= g(z), \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (22)$$

we find

$$\varphi(\theta) = \psi(z) = \frac{A + 2\,Bz + Cz^2}{a + 2\,bz + cz^2} = \frac{G(z)}{g(z)} \quad \ldots\ldots \quad (23)$$

Now we have

$$\frac{d\psi}{dz} = \frac{g\dfrac{dG}{dz} - G\dfrac{dg}{dz}}{g^2} = \frac{1}{g^2}\begin{vmatrix} g & \dfrac{dg}{dz} \\ G & \dfrac{dG}{dz} \end{vmatrix} = \frac{2}{g^2}\begin{vmatrix} a + 2\,bz + cz^2, & b + cz \\ A + 2\,Bz + Cz^2, & B + Cz \end{vmatrix}$$

$$= \frac{2}{g^2}\begin{vmatrix} a + bz, & b + cz \\ A + Bz, & B + Cz \end{vmatrix}.$$

So the value z_0 which minimizes $\psi(z)$, is one of the roots of the equation

$$\begin{vmatrix} a + bz, & b + cz \\ A + Bz, & B + Cz \end{vmatrix} = 0, \quad \ldots\ldots\ldots \quad (24)$$

or

$$(aB - bA) - (cA - aC)\,z + (bC - cB)\,z^2 = 0, \quad \ldots\ldots \quad (24')$$

for which we, putting

$$\left.\begin{aligned} bC - cB &= \alpha \\ cA - aC &= \beta \\ aB - bA &= \gamma \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (25)$$

can write

$$\alpha z^2 - \beta z + \gamma = 0. \quad \ldots\ldots\ldots \quad (24'')$$

The corresponding value of ψ is

$$\psi(z_0) = \psi_0 = \frac{G(z_0)}{g(z_0)} = \frac{G_0}{g_0} = \frac{(A + Bz_0) + (B + Cz_0)\,z_0}{(a + bz_0) + (b + cz_0)\,z_0},$$

or, by (24),

$$\psi_0 = \frac{A + Bz_0}{a + bz_0} = \frac{B + Cz_0}{b + cz_0} \quad \ldots \ldots \quad (25)$$

Hence

$$z_0 = -\frac{a\psi_0 - A}{b\psi_0 - B} = -\frac{b\psi_0 - B}{c\psi_0 - C} \quad \ldots \ldots \quad (26)$$

so that ψ_0 is a root of the equation

$$\begin{vmatrix} a\psi - A \;, & b\psi - B \\ b\psi - B \;, & c\psi - C \end{vmatrix} = 0, \quad \ldots \ldots \quad (27)$$

or

$$(ac - b^2)\,\psi^2 - (aC - 2\,bB + cA)\,\psi + (AC - B^2) = 0, \ldots \quad (27')$$

or, putting for abbreviation's sake

$$ac - b^2 = s \quad , \quad AC - B^2 = S \quad , \quad aC - 2\,bB + cA = \sigma, \ldots \quad (28^a)$$

$$s\,.\,\psi^2 - \sigma\,.\,\psi + S = 0 \quad \ldots \ldots \quad (27'')$$

From $s > 0$, $S > 0$, $a > 0$, $A > 0$ follows

$$b < \sqrt{ac} \quad , \quad B < \sqrt{AC} \quad , \quad \text{thus } bB < \sqrt{ac\,AC},$$

therefore

$$\sigma = aC - 2\,bB + cA = (\sqrt{aC} - \sqrt{cA})^2 + 2\,(\sqrt{ac\,AC} - bB) > 0.$$

The solution of (27''):

$$\psi = \frac{\sigma \pm \sqrt{\sigma^2 - 4\,sS}}{2s}$$

requires an investigation of the eliminant of $g\,(z)$ and $G\,(z)$:

$$\left.\begin{aligned} R = \sigma^2 - 4\,sS &= (aC - 2\,bB + cA)^2 - 4\,(ac - b^2)\,(AC - B^2) \\ &= (cA - aC)^2 - 4\,(bC - cB)\,(aB - bA) \\ &= \beta^2 - 4\,\alpha\gamma. \end{aligned}\right\} \quad (28^b)$$

$$\begin{aligned} R = \sigma^2 - 4\,sS &= \{(\sqrt{aC} - \sqrt{cA})^2 + 2\,(\sqrt{ac\,AC} - bB)\}^2 - 4\,(ac - b^2)\,(AC - B^2) \\ &= (\sqrt{aC} - \sqrt{cA})^4 + 4\,(\sqrt{aC} - \sqrt{cA})^2\,(\sqrt{ac\,AC} - bB) + \\ &\quad + 4\,(ac\,AC - 2bB\sqrt{ac\,AC} + b^2B^2 - ac\,AC + b^2\,AC + B^2\,ac - b^2\,B^2) \\ &= (\sqrt{aC} - \sqrt{cA})^4 + 4\,(\sqrt{aC} - \sqrt{cA})^2\,(\sqrt{ac\,AC} - bB) + \\ &\qquad\qquad + 4\,(b\sqrt{AC} - B\sqrt{ac})^2 > 0. \end{aligned}$$

Hence the roots of (27'') are real.

Obviously the minimum value ψ_0 of ψ is the inferior root of (27''), thus:

$$\psi_0 = \frac{\sigma - \sqrt{R}}{2s} \quad \ldots \ldots \quad (29)$$

The corresponding value z_0 of z is that root of (24″) which answers to ψ_0; it follows also from (26):

$$z_0 = \frac{-ac\,\psi_0 + cA}{cb\,\psi_0 - cB} = \frac{-b^2\psi_0 + bB}{bc\,\psi_0 - bC} = \frac{-(ac - b^2)\,\psi_0 + (cA - bB)}{bC - cB}$$

$$= \frac{-2\,s\,\psi_0 + 2\,(cA - bB)}{2\,a} = \frac{-\sigma + \sqrt{R} + 2\,(cA - bB)}{2\,a} =$$

$$= \frac{-cA + 2\,bB - aC + 2\,cA - 2\,bB + \sqrt{R}}{2\,a},$$

or

$$z_0 = \frac{\beta + \sqrt{R}}{2\,a} \quad \ldots\ldots\ldots\ldots \quad (30)$$

Hence the value of z required is, with the definitions for α, β and γ given in (25), the root of (24″) having the positive root of R.

The angle θ_0 required is therefore determined by

$$\operatorname{tg}\theta_0 = \frac{\beta + \sqrt{R}}{2\,a} = \frac{(cA - aC) + \sqrt{(cA - aC)^2 - 4\,(bC - cB)\,(aB - bA)}}{2\,(bC - cB)}. \quad (30')$$

So the angle θ_0 is known, all but 180°; we must choose that value of θ_0, which, being substituted in (21), makes l_0 positive.

In the formula (30′) for θ_0 the coefficients a, b, c, being functions of P, Q and ω, are given a priori, thus independent of the result of the experiment, which furnishes the pairs of numbers (x_k, y_k) $(k = 1, \ldots n)$. On the contrary the magnitudes A, B, C are really dependent of this result; so are the magnitudes $\bar{x}, \bar{y}$ appearing in the formula (21) for l_0. Repeating the proof, we can expect other values of $A, B, C, \bar{x}, \bar{y}$.

The values of θ and l obtained in (30′) and (21) by taking the average, furnish L_0 as the „apparent line" (apparently true line), on which the points S_k ought to lie. According to usage, we shall call the deviations of the points S_k from this line: the apparent errors (residuals) of the position of S_k. T_k being the point on L_0 corresponding to S_k, $\overrightarrow{T_k S_k} = -\delta_k$ is the apparent error of S_k, as to amount and as to direction.

Denoting the coordinates of T_k by X_k, Y_k, we have

$$X_k \cos\theta_0 + Y_k \sin\theta_0 - l_0 = 0.$$

The residuals of the coordinates of S_k being

$$x_k - X_k = \xi_k\,,\; y_k - Y_k = \eta_k, \quad \ldots\ldots\ldots \quad (31)$$

and the coordinates of S_k satisfying

$$x_k \cos\theta_0 + y_k \sin\theta_0 - l_0 = \lambda_k,$$

we find:

$$\xi_k \cos\theta_0 + \eta_k \sin\theta_0 = \lambda_k \quad \ldots\ldots\ldots \quad (32)$$

Passing to the system of coordinates of the main directions of elasticity (x', y'), the residuals ξ', η' of the coordinates of this system are connected to ξ, η by

$$\left.\begin{aligned}\xi &= \xi' \cos\omega - \eta' \sin\omega,\\ \eta &= \xi' \sin\omega + \eta' \cos\omega.\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (33)$$

As the moduli of elasticity P and Q (cf. (8)) play the part of "weights", P and Q are inversely proportional to the squares of the mean errors of x' and y', hence to the mean squares $\overline{\xi'^2}$ and $\overline{\eta'^2}$ of ξ' and η' resp.; moreover $\overline{\xi'\eta'}=0$, ξ' and η' being measured along the main directions of elasticity.

So we have

$$P\,.\,\overline{\xi'^2}=Q\,.\,\overline{\eta'^2},\quad \overline{\xi'\eta'}=0, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (34)$$

whence

$$\overline{\xi'^2}=\varrho\,Q,\quad \overline{\eta'^2}=\varrho\,P,\quad \overline{\xi'\eta'}=0; \quad . \; . \; . \; . \; . \; . \quad (34')$$

where ϱ is a factor of proportionality to be determined afterwards.

From (33) follows

$$\overline{\xi^2}=\overline{\xi'^2}\cos^2\omega - 2\,\overline{\xi'\eta'}\sin\omega\cos\omega + \overline{\eta'^2}\sin^2\omega = \varrho\,(Q\cos^2\omega + P\sin^2\omega),$$

$$\overline{\xi\eta}=\overline{\xi'^2}\sin\omega\cos\omega + \overline{\xi'\eta'}\,(\cos^2\omega - \sin^2\omega) - \overline{\eta'^2}\sin\omega\cos\omega = \varrho(Q-P)\sin\omega\cos\omega,$$

$$\overline{\eta^2}=\overline{\xi'^2}\sin^2\omega + 2\,\overline{\xi'\eta'}\sin\omega\cos\omega + \overline{\eta'^2}\cos^2\omega = \varrho\,(Q\sin^2\omega + P\cos^2\omega),$$

hence, on account of (11):

$$\overline{\xi^2}=\varrho\,a,\quad \overline{\xi\eta}=\varrho\,b,\quad \overline{\eta^2}=\varrho\,c. \quad . \; . \; . \; . \; . \; . \; . \quad (35)$$

By taking the mean squares of both sides of (32) we find

$$\overline{\xi^2}\cos^2\theta_0 + 2\,\overline{\xi\eta}\cos\theta_0\sin\theta_0 + \overline{\eta^2}\sin^2\theta_0 = \overline{\lambda^2},$$

thus, by (35),

$$\varrho\,(a\cos^2\theta_0 + 2\,b\cos\theta_0\sin\theta_0 + c\sin^2\theta_0) = \overline{\lambda^2},$$

whence, on account of (12) and of (14),

$$\varrho\,f(\theta_0) = (\overline{\lambda^2})_0 = \varphi_0\cdot f(\theta_0);$$

therefore

$$\varrho = \varphi_0 = \varphi\,(\theta_0) = \psi_0 = \psi\,(z_0) \quad . \; . \; . \; . \; . \; . \quad (36)$$

and

$$\overline{\xi^2}=\varphi_0\,a,\quad \overline{\xi\eta}=\varphi_0\,b,\quad \overline{\eta^2}=\varphi_0\,c, \quad . \; . \; . \; . \; . \; . \quad (37)$$

$\varphi_0=\psi_0$ being determined by (29).

In this way the mean squares and the mean product of the residuals are found.

Denoting the true errors of x_k, y_k, u_k, v_k, $\bar{x}$, $\bar{y}$, etc. by $\triangle x_k$, $\triangle y_k$, etc., the formula

$$u_k = x_k - \bar{x} = x_k - \frac{x_1+x_2+\ldots+x_k+\ldots+x_n}{n} = \frac{-x_1-x_2-\ldots+(n-1)x_k-\ldots-x_n}{n}$$

gives

$$\triangle u_k = \frac{-\triangle x_1 - \triangle x_2 - \ldots + (n-1)\triangle x_k - \ldots - \triangle x_n}{n} \quad . \; . \quad (38^a)$$

Likewise

$$\triangle v_k = \frac{-\triangle y_1 - \triangle y_2 - .. + (n-1)\,\triangle y_k - .. - \triangle y_n}{n} \quad . \quad . \quad (38^b)$$

The errors of $A = \frac{[uu]}{n}$, $B = \frac{[uv]}{n}$, $C = \frac{[vv]}{n}$ are:

$$\triangle A = \frac{2}{n}[u\triangle u],\ \triangle B = \frac{1}{n}\{[v\triangle u] + [u\triangle v]\},\ \triangle C = \frac{2}{n}[v\triangle v].$$

In determining the mean error of a function of A, B and C, we have to do with the mean values of $\triangle A^2$, $\triangle A \triangle B$, $\triangle A \triangle C$, $\triangle B^2$, $\triangle B \triangle C$, $\triangle C^2$, thus with the mean values of the squares and products built up out of $[u\triangle u]$, $[v\triangle u]$, $[u\triangle v]$, $[v\triangle v]$.

In computing the mean value of $[u\triangle u]^2$ for instance, we meet with two sums, viz.: $[u_k u_k . \triangle u_k \triangle u_k]$ and $[[u_k u_l . \triangle u_k \triangle u_l]]$, where $[[\ \ ]]$ designates a summation of the $n(n-1)$-terms wherein $l \neq k$.

The errors $\triangle u_k$, $\triangle v_k$ being supposed independent of the very u_k, v_k, the mean value of $[u_k u_k . \triangle u_k \triangle u_k]$, represented by $M([u_k u_k . \triangle u_k \triangle u_k])$, may be written:

$$M([u_k u_k . \triangle u_k \triangle u_k]) = M([u_k u_k]) \times M(\triangle u_k \triangle u_k);$$

likewise

$$M([[u_k u_l . \triangle u_k \triangle u_l]]) = M([[u_k u_l]]) \times M(\triangle u_k \triangle u_l).$$

Now

$$[u_k u_k] = nA,\ [u_k]^2 = [u_k u_k] + [[u_k u_l]] = 0, \text{ thus } [[u_k u_l]] = -nA.$$

likewise

$$[u_k v_k] = nB,\ [u_k][v_k] = [u_k v_k] + [[u_k v_l]] = 0, \text{ thus } [[u_k v_l]] = -nB,$$

$$[v_k v_k] = nC,\ [v_k]^2 = [v_k v_k] + [[v_k v_l]] = 0, \text{ thus } [[v_k v_l]] = -nC.$$

Moreover:

$$\left.\begin{aligned} \triangle u_1 &= \frac{(n-1)\,\triangle x_1 - \triangle x_2 - \triangle x_3 - .. - \triangle x_n}{n}, \\ \triangle u_2 &= \frac{-\triangle x_1 + (n-1)\,\triangle x_2 - \triangle x_3 - .. - \triangle x_n}{n} \end{aligned}\right\} \quad . \quad . \quad (38c)$$

whence

$$\triangle u_1 \triangle u_1 = \frac{1}{n^2}\{+(n-1)^2 \triangle x_1^2 + \triangle x_2^2 + \triangle x_3^2 + .. + \triangle x_n^2 + [[p_{kl} \triangle x_k \triangle x_l]]\}$$

$$\triangle u_1 \triangle u_2 = \frac{1}{n^2}\{-(n-1)\triangle x_1^2 - (n-1)\triangle x_2^2 + \triangle x_3^2 + .. + \triangle x_n^2 + [[q_{kl} \triangle x_k \triangle x_l]]\}.$$

Now we have

$$M(\triangle x_1^2) = M(\triangle x_2^2) = .. = M(\triangle x_n^2) = M(\triangle x^2),\ M(\triangle x_k \triangle x_l) = 0 \text{ (for } l \neq k),$$

therefore

$$M(\triangle u_1 \triangle u_1) = \frac{1}{n^2}\{(n-1)^2 M(\triangle x_1^2) + (n-1)\ M(\triangle x^2)\} = \frac{n-1}{n} M(\triangle x^2),$$

$$M(\triangle u_1 \triangle u_2) = \frac{1}{n^2}\{-(n-1) M(\triangle x_1^2) - (n-1) M(\triangle x_2^2) + (n-2) M(\triangle x^2)\} =$$

$$= -\frac{1}{n} M(\triangle x^2).$$

Hence:

$$M(\triangle u_k \triangle u_k) = \frac{n-1}{n} M(\triangle x^2), \quad M(\triangle u_k \triangle u_l) = -\frac{1}{n} M(\triangle x^2).$$

Likewise:

$$M(\triangle u_k \triangle v_k) = \frac{n-1}{n} M(\triangle x \triangle y), \quad M(\triangle u_k \triangle v_l) = -\frac{1}{n} M(\triangle x \triangle y).$$

$$M(\triangle v_k \triangle v_k) = \frac{n-1}{n} M(\triangle y^2), \quad M(\triangle v_k \triangle v_l) = -\frac{1}{n} M(\triangle y^2).$$

So we arrive at

$$\begin{aligned} M([u\triangle u]^2) &= M([u_k u_k \,.\, \triangle u_k \triangle u_k] + [[u_k u_l \,.\, \triangle u_k \triangle u_l]]) = \\ &= M([u_k u_k]) \,.\, M(\triangle u_k \triangle u_k) + M([[u_k u_l]]) \,.\, M(\triangle u_k \triangle u_l) \\ &= nM(A) \,.\, \frac{n-1}{n} M(\triangle x^2) - nM(A) \times -\frac{1}{n} M(\triangle x^2) = \\ &= nM(A) \,.\, M(\triangle x^2). \end{aligned}$$

Likewise:

$$\begin{aligned} &M([u\triangle u]\,[u\triangle v]) = nM(A) \,.\, M(\triangle x \triangle y), \\ &M([u\triangle v]^2) = nM(A) \,.\, M(\triangle y^2), \\ &M([u \triangle u]\,[v \triangle u]) = n\,M(B) \,.\, M(\triangle x^2), \\ &M([u \triangle u]\,[v \triangle v]) = M([u \triangle v]\,[v \triangle u]) = n\,M(B) \,.\, M(\triangle x \triangle y), \\ &M([u \triangle v]\,[v\triangle v]) = n\,M(B) \,.\, M(\triangle y^2), \\ &M([v \triangle u]^2) = n\,M(C) \,.\, M(\triangle x^2), \\ &M([v \triangle u]\,[v \triangle v]) = n\,M(C) \,.\, M(\triangle x \triangle y), \\ &M([v \triangle v]^2) = n\,M(C) \,.\, M(\triangle y^2). \end{aligned}$$

By means of these formulae we find

$$M(\triangle A^2) = \frac{4}{n^2} M([u \triangle u]^2) = \frac{4}{n} M(A) \,.\, M(\triangle x^2),$$

$$\begin{aligned} M(\triangle A \,.\, \triangle B) &= \frac{2}{n^2} M([u \triangle u]\,\{[v \triangle u] + [u \triangle v]\}) = \\ &= \frac{2}{n} \{M(B) \,.\, M(\triangle x^2) + M(A) \,.\, M(\triangle x \triangle y)\}, \end{aligned}$$

$$M(\triangle A \triangle C) = \frac{4}{n^2} M([u \triangle u]\,[v\triangle v]) = \frac{4}{n} M(B) \,.\, M(\triangle x \triangle y),$$

$$\begin{aligned} M(\triangle B^2) &= \frac{1}{n^2} M(\{[v \triangle u] + [u \triangle v]\}^2) = \\ &= \frac{1}{n} \{M(C) \,.\, M(\triangle x^2) + 2\,M(B) \,.\, M(\triangle x \triangle y) + M(A) \,.\, M(\triangle y^2)\}, \end{aligned}$$

$$\begin{aligned} M(\triangle B \triangle C) &= \frac{2}{n^2} M(\{[v \triangle u) + [u \triangle v]\}\,[v \triangle v]) = \\ &= \frac{2}{n} \{M(C) \,.\, M(\triangle x \triangle y) + M(B) \,.\, M(\triangle y^2)\}, \end{aligned}$$

$$M(\triangle C^2) = \frac{4}{n^2} M([v \triangle v]^2) = \frac{4}{n} M(C) \,.\, M(\triangle y^2).$$

As the present problem of adjustment deals with two unknowns (θ and l), so that there is only question of adjustment if $n > 2$, the formula for the square of the mean true error runs:

$$\mathsf{E}^2(x) = M(\triangle x^2) = \frac{[\xi^2]}{n-2} = \frac{n\overline{\xi^2}}{n-2} = \frac{n}{n-2}\varphi_0\, a.$$

Likewise:

$$\left.\begin{aligned} M(\triangle x \triangle y) &= \frac{[\xi\eta]}{n-2} = \frac{n\overline{\xi\eta}}{n-2} = \frac{n}{n-2}\varphi_0\, b, \\ \mathsf{E}^2(y) = M(\triangle y^2) &= \frac{[\eta^2]}{n-2} = \frac{n\overline{\eta^2}}{n-2} = \frac{n}{n-2}\varphi_0\, c. \end{aligned}\right\} \quad \ldots \quad (39)$$

Replacing moreover the values $M(A)$, $M(B)$, $M(C)$, essentially unknown, by the values A, B, C actually found, we obtain

$$\left.\begin{aligned} M(\triangle A^2) &= \frac{4\varphi_0}{n-2}\cdot aA, \\ M(\triangle A\triangle B) &= \frac{2\varphi_0}{n-2}\cdot(aB + bA), \\ M(\triangle A\triangle C) &= \frac{4\varphi_0}{n-2}\cdot bB, \\ M(\triangle B^2) &= \frac{\varphi_0}{n-2}\cdot(aC + 2\,bB + cA), \\ M(\triangle B\triangle C) &= \frac{2\varphi_0}{n-2}\cdot(bC + cB), \\ M(\triangle C^2) &= \frac{4\varphi_0}{n-2}\cdot cC. \end{aligned}\right\} \quad \ldots\ldots \quad (40)^{1)}$$

As $\theta_0 = \operatorname{arc\,tg} z_0$, by (24″), is a function of α, β and γ, the mean error of θ_0 (and of z_0) will be built up out of the means

$$M(\triangle\alpha^2) \quad , \quad M(\triangle\alpha\triangle\beta), \ldots \text{ etc.}$$

We have

$$\triangle\alpha = b\triangle C - c\triangle B, \quad \triangle\beta = c\triangle A - a\triangle C, \quad \triangle\gamma = a\triangle B - b\triangle A,$$

thus:

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1) The formulae (40) differ from the formulae $M(\triangle A^2) = \frac{2A^2}{n-1}$, $M(\triangle A\triangle B) = \frac{2AB}{n-1}$, $M(\triangle A\triangle C) = \frac{2B^2}{n-1}$, $M(\triangle B^2) = \frac{B^2 + AC}{n-1}$, $M(\triangle B\triangle C) = \frac{2BC}{n-1}$, $M(\triangle C^2) = \frac{2C^2}{n-1}$, valid in the case of linear correlation between x and y. In the case of correlation between x and y the deviations u_k and v_k of x_k and y_k from $\bar{x}$ and $\bar{y}$ are considered as accidental errors. In the present case however the coordinates x_k and y_k are yet considered as free from error, provided the point S_k be situated on L_0.

$$M(\triangle\alpha^2) = b^2\, M(\triangle C^2) - 2bc\, M(\triangle B\,\triangle C) + c^2\, M(\triangle B^2)$$

$$= \frac{\varphi_0}{n-2}\{b^2 \,.\, 4cC - 2\,bc \,.\, 2\,(bC + cB) + c^2\,(aC + 2\,bB + cA)\} =$$

$$= \frac{\varphi_0}{n-2}\, c^2\,(aC - 2\,bB + cA),$$

$$M(\triangle\alpha\,\triangle\beta) = bcM(\triangle A\triangle C) - c^2M(\triangle A\triangle B) - abM(\triangle C^2) + acM(\triangle B\triangle C)$$

$$= \frac{\varphi_0}{n-2}\{bc\,.\,4\,bB - c^2\,.\,2(aB + bA) - ab\,.\,4\,cC + ac\,.\,2\,(bC + cB)\} =$$

$$= \frac{-2\,\varphi_0}{n-2}\, bc\,(aC - 2\,bB + cA),$$

$$M(\triangle\alpha\,\triangle\gamma) = abM(\triangle B\,\triangle C) - b^2M(\triangle A\,\triangle C) - acM(\triangle B^2) + bcM(\triangle A\,\triangle B)$$

$$= \frac{\varphi_0}{n-2}\{ab.2(bC + cB) - b^2.4bB - ac(aC + 2bB + cA) + bc.2(aB + bA)\} =$$

$$= \frac{\varphi_0}{n-2}\,(2\,b^2 - ac)\,(aC - 2\,bB + cA),$$

$$M(\triangle\beta^2) = c^2M(\triangle A^2) - 2\,acM(\triangle A\,\triangle C) + a^2M(\triangle C^2)$$

$$= \frac{\varphi_0}{n-2}\{c^2.\,4aA - 2ac\,.\,4b\,B + a^2.\,4cC\} = \frac{4\varphi_0}{n-2}\,ac\,(aC - 2bB + cA),$$

$$M(\triangle\beta\,\triangle\gamma) = acM(\triangle A\,\triangle B) - bcM(\triangle A^2) - a^2M(\triangle B\,\triangle C) + abM(\triangle A\,\triangle C)$$

$$= \frac{\varphi_0}{n-2}\{ac.2(aB + bA) - bc.4aA - a^2.2(bC + cB) + ab.4bB\} =$$

$$= \frac{-2\varphi_0}{n-2}\, ab\,(aC - 2\,bB + cA),$$

$$M(\triangle\gamma^2) = a^2\, M(\triangle B^2) - 2\,ab\, M(\triangle A\,\triangle B) + b^2\, M(\triangle A^2)$$

$$= \frac{\varphi_0}{n-2}\{a^2\,(aC + 2\,bB + cA) - 2\,ab\,.\,2\,(aB + bA) + b^2.\,4\,aA\} =$$

$$= \frac{\varphi_0}{n-2}\, a^2\,(aC - 2\,bB + cA),$$

or, on account of (28^a),

$$\left.\begin{array}{ll}
M(\triangle\alpha^2) = \dfrac{\varphi_0\sigma}{n-2}\,.\,c^2, & M(\triangle\alpha\triangle\beta) = \dfrac{-2\varphi_0\sigma}{n-2}\,.\,bc, \\
 & M(\triangle\alpha\,\triangle\gamma) = \dfrac{\varphi_0\sigma}{n-2}\,.\,(2\,b^2 - ac), \\
M(\triangle\beta^2) = \dfrac{4\,\varphi_0\sigma}{n-2}\,.\,ac, & M(\triangle\beta\triangle\gamma) = \dfrac{-2\varphi_0\,\sigma}{n-2}\,.\,ab, \\
 & M(\triangle\gamma^2) = \dfrac{\varphi_0\sigma}{n-2}\,.\,a^2.
\end{array}\right\} \quad (41)$$

Taking z_0 as central value, we derive from (24''):

$$2\,\alpha z_0 \triangle z_0 - \beta \triangle z_0 + z_0^2 \triangle \alpha - z_0 \triangle \beta + \triangle \gamma = 0$$

or

$$-(2\,\alpha z_0 - \beta)\triangle z_0 = z_0^2 \triangle \alpha - z_0 \triangle \beta + \triangle \gamma \quad . \quad . \quad . \quad . \qquad (42)$$

whence

$$(2\,\alpha z_0 - \beta)^2 M(\triangle z_0^2) = z_0^4 M(\triangle \alpha^2) - 2\,z_0^3 M(\triangle \alpha \triangle \beta) + \\ + 2\,z_0^2 M(\triangle \alpha \triangle \gamma) + z_0^2 M(\triangle \beta^2) - 2\,z_0 M(\triangle \beta \triangle \gamma) + M(\triangle \gamma^2)$$

Now

$$(2\,\alpha z_0 - \beta)^2 = 4\,\alpha\,(\alpha z_0^2 - \beta z_0 + \gamma) + (\beta^2 - 4\,\alpha\gamma),$$

or, z_0 being a root of (24''), and by (28^b),

$$(2\,\alpha z_0 - \beta)^2 = R.$$

Substituting for $M(\triangle \alpha^2)$ etc. the values found in (41), we obtain

$$R\,.\,M(\triangle z_0^2) = \frac{\varphi_0\sigma}{n-2}\{z_0^4\,.\,c^2 - 2\,z_0^3\,.\,-2\,bc + 2\,z_0^2\,.\,(2\,b^2 - ac) + \\ + z_0^2\,.\,4\,ac - 2\,z_0\,.\,-2\,ab + a^2\}$$

$$= \frac{\varphi_0\sigma}{n-2}(c\,z_0^2 + 2\,bz_0 + a)^2,$$

or, by (22) and (23),

$$M(\triangle z_0^2) = \frac{\varphi_0\sigma}{(n-2)\,R}\{\,g(z_0)\,\}^2 = \frac{\sigma\varphi_0 g_0^2}{(n-2)\,R} = \frac{\sigma g_0 G_0}{(n-2)\,R}.$$

We have further for the true error of θ_0:

$$\triangle\,\theta_0 = \frac{\triangle z_0}{1 + z_0^2},$$

thus

$$M(\triangle \theta_0^2) = \frac{M(\triangle z_0^2)}{(1+z_0^2)^2} = \frac{\sigma\varphi_0}{(n-2)\,R}\left(\frac{g_0}{1+z_0^2}\right)^2 =$$

$$= \frac{\sigma\varphi_0}{(n-2)R}\left(\frac{a + 2\,b\,\mathrm{tg}\,\theta_0 + c\,\mathrm{tg}^2\,\theta_0}{\sec^2\theta_0}\right)^2 =$$

$$= \frac{\sigma\varphi_0}{(n-2)\,R}(a\cos^2\theta_0 + 2\,b\cos\theta_0\sin\theta_0 + c\sin^2\theta_0)^2 =$$

$$= \frac{\sigma\varphi_0}{(n-2)\,R}\{f(\theta_0)\}^2 = \frac{\sigma f_0 F_0}{(n-2)\,R}.$$

So the square of the mean true error $\mathrm{E}(\theta_0)$ of θ_0 is

$$\mathrm{E}^2(\theta_0) = \frac{1}{n-2}\cdot\frac{\sigma}{R}\cdot f_0 F_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (43)$$

The mean error of l_0 is to be derived from

$$\triangle\,l_0 = \triangle\,\bar{x}\,.\cos\theta_0 + \triangle\bar{y}\,.\sin\theta_0 + (-\,\bar{x}\sin\theta_0 + \bar{y}\cos\theta_0)\triangle\,\theta_0.$$

Here we have (see (42))

$$\triangle\,\theta_0=\frac{\triangle z_0}{1+z_0^2}=-\frac{z_0^2\,\triangle\,\alpha-z_0\,\triangle\,\beta+\triangle\,\gamma}{(1+z_0^2)\,(2\,\alpha z_0-\beta)}=$$

$$=-\frac{z_0^2\,(b\triangle C-c\triangle B)-z_0(c\triangle A-a\triangle C)+(a\triangle B-b\triangle A)}{(1+z_0^2)\,(2\alpha z_0-\beta)}$$

$$=\lambda\,\triangle\,A+\mu\,\triangle\,B+\nu\,\triangle\,C.$$

So we obtain:

$$\left.\begin{aligned}M\,(\triangle l_0^2)=\cos^2\theta_0\,.\,M\,(\triangle\,\overline{x}^2)+2\cos\theta_0\sin\theta_0\,.\,M\,(\triangle\overline{x}\triangle\overline{y})+\\+\sin^2\theta_0\,.\,M(\triangle y^2)+2\,(-x\sin\theta_0+\overline{y}\cos\theta_0)\,\{\cos\theta_0\,.\,M(\triangle\overline{x}\triangle\theta_0)+\\+\sin\theta_0\,.\,M\;(\triangle\overline{y}\,\triangle\,\theta_0)\,\}+(-\,\overline{x}\sin\theta_0+\overline{y}\cos\theta_0)^2\,M\,(\triangle\theta_0^2).\end{aligned}\right\}\quad(44)$$

Now from

$$\overline{x}=\frac{[x]}{n},\quad y=\frac{[y]}{n}$$

ensues

$$M\,(\triangle\overline{x}^2)=\frac{1}{n}\,M(\triangle x^2),\;M(\triangle x\triangle y)=\frac{1}{n}\,M(\triangle x\triangle y),\quad M(\triangle\overline{y}^2)=\frac{1}{n}\,M\,(\triangle y^2),$$

hence, by (39),

$$M\,(\triangle x^2)=\frac{\varphi_0 a}{n-2},\;M\,(\triangle\overline{x}\triangle y)=\frac{\varphi_0 b}{n-2},\;M\,(\triangle\overline{y}^2)=\frac{\varphi_0 c}{n-2}\quad.\quad(45)$$

Moreover:

$$M\,(\triangle x\triangle\theta_0)=\lambda M\,(\triangle\overline{x}\triangle A)+\mu M\,(\triangle\overline{x}\triangle B)+\nu M\,(\triangle\overline{x}\triangle C);$$

likewise:

$$M\,(\triangle\overline{y}\triangle\theta_0)=\lambda M\,(\triangle\overline{y}\triangle A)+\mu M\,(\triangle\overline{y}\triangle B)+\nu M\,(\triangle\overline{y}\triangle C).$$

Now

$$M\,(\triangle\overline{x}\triangle A)=\frac{2}{n^2}\,M\,([\triangle x]\,[u\triangle u])=\frac{2}{n^2}M\,([u_k\triangle u_k\triangle x_k]+[[u_k\triangle u_k\triangle x_l]])$$

$$=\frac{2}{n^2}\,\{\,M\,([u_k])\,M\,(\triangle u_k\triangle x_k)+M\,[[u_k]]\,M\,(\triangle u_k\triangle x_l)\,\}.$$

As however $[u_k]=0$, also $M\,([u_k])=0$; therefore:

$$M\,(\triangle\overline{x}\,.\,\triangle A)=0;$$

likewise

$$M\,(\triangle\overline{x}\,.\,\triangle B)=0,\quad M\,(\triangle\overline{x}\,.\,\triangle C)=0,\quad M\,(\triangle\overline{y}\,.\,\triangle\,A)=0,$$

$$M\,(\triangle\overline{y}\,.\,\triangle B)=0,\;M\,(\triangle\overline{y}\,.\,\triangle C)=0,$$

whence

$$M\,(\triangle\overline{x}\,.\,\triangle\theta_0)=0,\;M\,(\triangle\overline{y}\,.\,\triangle\theta_0)=0.\quad.\quad.\quad.\quad.\quad(46)$$

In virtue of (44), (45), (46) and (43), we find at last for $M\,(\triangle l_0^2) = \mathrm{E}^2\,(l_0)$:

$$\begin{aligned}\mathrm{E}^2\,(l_0) &= \frac{\varphi_0}{n-2}\left\{ a\cos^2\theta_0 + 2\,b\cos\theta_0\sin\theta_0 + c\sin^2\theta \right\} + \\ &\qquad + (-\bar{x}\sin\theta_0 + \bar{y}\cos\theta_0)^2 \,.\, \frac{1}{n-2}\cdot\frac{\sigma}{R} f_0\,F_0 \\ &= \frac{\varphi_0 f_0}{n-2} + (\bar{x}^2 + \bar{y}^2 - l_0^2)\,.\,\frac{1}{n-2}\cdot\frac{\sigma}{R}\cdot f_0\,F_0,\end{aligned}$$

or

$$\mathrm{E}^2\,(l_0) = \frac{F_0}{n-2}\left\{ 1 + (\bar{x}^2 + \bar{y}^2 - l_0^2)\,.\,\frac{\sigma}{R} f_0 \right\} \quad . \quad . \quad . \quad . \quad (47)$$

Here $\bar{x}^2 + \bar{y}^2 - l_0^2$ represents the square of the projection p of the radius vector of the "mean point" $(\bar{x}, \bar{y})$ on the line L_0.

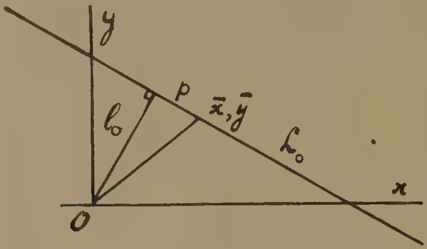

Fig. 2.

Hence

$$\mathrm{E}^2\,(l_0) = \frac{F_0}{n-2}\left\{ 1 + p^2 \frac{\sigma}{R} f_0 \right\} \quad . \quad . \quad . \quad\quad . \quad . \quad (47')$$

Moreover we have, in virtue of (46),

$$\left.\begin{aligned} M(\triangle\, l_0 \triangle\, \theta_0) &= (-\bar{x}\sin\theta_0 + \bar{y}\cos\theta_0)\; M\,(\triangle\,\theta_0^2) = \\ &= \frac{1}{n-2}\cdot\frac{\sigma}{R}\cdot f_0\,F_0 \,.\, (-\bar{x}_0\sin\theta_0 + \bar{y}\cos\theta_0)\end{aligned}\right\} \quad . \quad (48)$$

If there is occasion to consider the different "observed points" $S_k\,(x_k,\,y_k)$ unequally certain, we can assign to each point S_k a weight g_k. Then we operate with $u'_k = u_k\sqrt{g_k}$, $v'_k = v_k\sqrt{g_k}$ and with $A' = \frac{[g_k\,u_k\,u_k]}{n} = \overline{guu}$, $B' = \frac{[g_k\,u_k\,v_k]}{n} = \overline{guv}$, $C' = \frac{[g_k\,v_k\,v_k]}{n} = \overline{gvv}$ in the same manner as we have operated above with u_k, v_k, A, B and C.

Summarising the results obtained above, we can say that the most probable line L_0

$$x\cos\theta_0 + y\sin\theta_0 - l_0 = 0$$

is determined by (30′) and (21), thus by

$$\operatorname{tg}\theta_0 = \frac{\beta + \sqrt{R}}{2\alpha}\;, \quad l_0 = \bar{x}\cos\theta_0 + \bar{y}\sin\theta_0 > 0,$$

the mean errors of θ_0 and l_0 being determined by (43) and (47′), thus by

$$\mathrm{E}^2(\theta_0)=\frac{1}{n-2}\cdot\frac{\sigma}{R}\cdot f_0\,F_0 \quad , \quad \mathrm{E}^2(l_0)=\frac{F_0}{n-2}\left\{1+p^2\cdot\frac{\sigma}{R}\cdot f_0\right\},$$

where

$$\alpha=bC-cB\ ,\ \beta=cA-aC\ ,\ \gamma=aB-bA\ ,\ \sigma=aC-2\,bB+cA,$$
$$R=\beta^2-4\,\alpha\gamma=(aC-2\,bB+cA)^2-4\,(ac-b^2)\,(AC-B^2),$$
$$f_0=a\cos^2\theta_0+2\,b\cos\theta_0\sin\theta_0+c\sin^2\theta_0\ ,\ F_0=A\cos^2\theta_0+$$
$$+\,2\,B\cos\theta_0\sin\theta_0+C\sin^2\theta_0.$$
$$p^2=\overline{x}^2+\overline{y}^2-l_0^2.$$

Particular cases.

I. The axes of coordinates coincide with the main axes of elasticity. Here we have $\omega=0$, thus $a=Q$, $b=0$, $c=P$, whence

$$\alpha=-PB\ ,\ \beta=PA-QC\ ,\ \gamma=QB\ ,\ \sigma=PA+QC,$$
$$R=(PA-QC)^2+4\,PQB^2=(PA+QC)^2-4\,PQ\,(AC-B^2),$$
$$f_0=Q\cos^2\theta_0+P\sin^2\theta_0.$$

$M(\triangle x\triangle y)=0$, so the errors of x and y are independent of each other.

II. The plane is isotropic, or, what comes to the same thing: x and y are equally uncertain.

Then we have $P=Q=1$, so that $a=c=1$, $b=0$, whence

$$\alpha=-B\ ,\ \beta=A-C\ ,\ \gamma=B\ ,\ \sigma=A+C,$$
$$R=(A-C)^2+4\,B^2=(A+C)^2-4\,(AC-B^2),$$
$$f_0=1.$$

Therefore

$$\mathrm{tg}\,\theta_0=\frac{A-C+\sqrt{(A-C)^2+4\,B^2}}{-2\,B}=\frac{C-A-\sqrt{(C-A)^2+4\,B^2}}{2\,B};$$

$$\mathrm{tg}\,2\,\theta_0=\frac{2\,B}{A-C}\ ,\ \cos 2\,\theta_0=\frac{C-A}{\sqrt{R}}\ ,\ \sin 2\,\theta_0=\frac{-2B}{\sqrt{R}};$$

$$\mathrm{E}^2(\theta_0)=\frac{1}{n-2}\cdot\frac{(A+C)F_0}{(A+C)^2-4\,(AC-B^2)},$$

$$\mathrm{E}^2(l_0)=\frac{F_0}{n-2}\left\{1+p^2\cdot\frac{A+C}{\sqrt{(A+C)^2-4\,(AC-B^2)}}\right\};$$

$$F_0=\frac{A+C}{2}+\frac{A-C}{2}\cos 2\theta_0+B\sin 2\theta_0=\frac{A+C-\sqrt{(A+C)^2-4(AC-B^2)}}{2}.\ ^{1)}$$

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1) The formula for tg θ_0 (and tg $2\theta_0$) is the same as in the case of linear correlation between the variables x_k, y_k. The expression for the mean error of θ_0 however is different (see the footnote on page 1032).

III. x is perfectly certain: $\frac{P}{Q} = \infty$, or $P = 1$, $Q = 0$.

So we have $a = b = 0$, $c = 1$, whence

$$\alpha = -B,\ \beta = A,\ \gamma = 0,\ \sigma = A,\ R = A^2;\ f_0 = \sin^2 \theta_0.$$

$\operatorname{tg} \theta_0 = \frac{2A}{-2B} = -\frac{A}{B}$, or, what comes to the same thing: the direction tangent of the line L_0 is $\frac{B}{A} = \frac{\overline{uv}}{\overline{uu}}$.

$$f_0 = \frac{1}{1 + \frac{B^2}{A^2}} = \frac{A^2}{A^2+B^2}, \quad F_0 = \frac{A + 2B \operatorname{tg} \theta_0 + C \operatorname{tg}^2\theta_0}{1 + \operatorname{tg}^2\theta_0} = \frac{A - 2A + \frac{A^2C}{B^2}}{1 + \frac{A^2}{B^2}} =$$

$$= \frac{A(AC - B^2)}{A^2 + B^2},$$

$$\mathrm{E}^2(\theta_0) = \frac{1}{n-2} \cdot \frac{1}{A} \frac{A^3(AC-B^2)}{(A^2+B^2)^2} = \frac{A^2(AC-B^2)}{(n-2)(A^2+B^2)^2}, \text{ or}$$

$$\mathrm{E}(\theta_0) = \frac{1}{\sqrt{n-2}} \cdot \frac{A\sqrt{AC-B^2}}{A^2+B^2};$$

$$\mathrm{E}^2(l_0) = \frac{A(AC-B^2)}{(n-2)(A^2+B^2)} \left\{ 1 + p^2 \cdot \frac{A}{A^2+B^2} \right\}. \text{ }^{1)}$$

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[1] Here we have the same case as that of n observational equations $mx_k + h = y_k$, where m and h are the unknowns, x_k the known (and perfectly exact) coefficients, y_k the observations. The solution of the normal equations $[xx]\,m + [x\,.\,1]\,h = [xy]$, $[x\,.\,1]\,m + [1 \times 1]\,h = [1\,.\,y]$ $([1 \times 1] = n)$ furnishes, after introducing $u_k = x_k - \bar{x}$, $v_k = y_k - \bar{y}$, the same expression for m, viz. $\frac{\overline{uv}}{\overline{uu}}$. We also find for $\theta = \operatorname{arc\,tg} m \pm \frac{\pi}{2}$ and $l = h \sin \theta = \frac{\pm h}{\sqrt{1+m^2}}$ the same mean errors as above.

Chemistry. — *The Influence of Pressure on the Reaction velocity, and the Function of the Medium.* By A. L. TH. MOESVELD and WILHELMA A. T. DE MEESTER. (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 24, 1927).

1. The investigations on the influence of pressure on the reaction velocity [1]) have taught that such an effect does exist, but have not yet led to connect this influence with other factors, or to formulate a theory on this phenomenon. We only know that the effect may be positive as well as negative, and may be very different in magnitude for apparently not greatly divergent reactions and external conditions. Any prediction as to the effect to be expected in cases which have not yet been investigated, has not been possible up to this time. We may indeed, from what was found, conclude that the influence of pressure is not secondary, at least in the main, in other words that the effects found are not the consequence of changes in viscosity or electrolytic dissociation degree by pressure, but that a more direct connection must exist between these and the reaction velocity. We are of opinion that now an endeavour may be made to draw up a theory on this influence of pressure, which theory is based on a more elaborate study about the function of the medium in reactions in solution. This theory has enabled us to give three predictions as to the connection of this influence of pressure and a number of modifications of the circumstances in which the reaction takes place; these predictions are corroborated by experiments. We intend to return to these experiments, which are not quite completed, in a later paper.

2. Before entering upon our subject one word more about the significance of this factor of pressure. It is well known that reaction velocities are very sensitive for most of the influences we can exercise. Change of temperature is very radical, but on this subject theory is already well advanced. It is different with the influence of the medium, which can be enormously great, and of which little can be said theoretically. It is for this

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[1]) ERNST COHEN and R. B. DE BOER, Zeitschr. f. physik. Chemie **84**, 41 (1913).
ERNST COHEN and H. F. G. KAISER, ibidem **89**, 338 (1915).
ERNST COHEN and A. M. VALETON, ibidem **92**, 433 (1917).
A. L. TH. MOESVELD, Verslagen Kon. Akad. v. Wet. Amsterdam, **31**, 195 (1922); Zeitschr. f. physik. Chemie **103**, 486 (1923).
A. L. TH. MOESVELD, Verslagen Kon. Akad. v. Wet. Amsterdam, **32**, 457 (1923); Zeitschr. f. physik. Chemie **105**, 455 (1923).
For the older investigations see: ERNST COHEN und W. SCHUT, Piezochemie kondensierter Systeme, Leipzig 1919, pag. 395.

reason that pressure as a variable has many advantages. This factor changes the reaction mixture but little. Temperature and medium remain as they were, only as a consequence of compression a slight change of concentration appears, which can be accurately computed. The change of viscosity and of some other factors can also be computed or estimated. When it appears that in some cases pressure has a considerable influence, it is possible that we may find a cause which is responsible for this, but which has not yet been thought of, or of which it was not supposed that the effect would be so predominating. If we wish to find out if we are on the right track in admitting this cause, we shall have to make predictions from this point of view and test them with experiments.

3. It has already been observed that a pretty clear idea may be formed of the influence of temperature in chemical reactions. Of great importance are in this case the "active" molecules, whose energy exceeds a certain "critical" value. In the first instance the distribution law of MAXWELL—BOLTZMANN dominates the distribution of energy, and the great change, with the temperature, of the number of molecules, which possesses more than a certain multiple of the mean energy at T goes parallel with the great influence of this temperature.

The difficulties with the mechanism of activation which have not yet been solved need not be entered upon here. It is sufficient to consider the partition of energy in the case of those gasreactions which are not disturbed by homogeneous and heterogeneous catalysis, but the difficulties begin as soon as we turn to reactions in solution. Except the very peculiar case of the dissociation of nitrogen pentoxide (N_2O_5), which in different media takes place with the same velocity as in the state of gas [1]), we have always to do with homogeneous catalysis, therefore with the influence of the medium on the reaction velocity. Cases are known, in which a reaction in one medium takes place millions of times more quickly than in another medium at the same temperature. If we take into consideration that also in the state of solution the mean kinetic energy depends only on temperature, we must, in order to explain these divergent reaction velocities, try to find factors which can change the number of the molecules that continuously obtain more than the critical energy, within wide limits at constant temperature. Neither can we call to aid the mechanism of activation, by supposing that the output of active molecules in different media is very variable, for the number of molecules in one and the same volume of different media and their magnitude lies within narrow limits, so that the number of collisions of these solvent molecules with those of the reacting substance(s) is likewise of the same order of magnitude. The mechanism of activation can, indeed, only play a part when it yields a number of activated molecules equal to the number of molecules that dissociate, but not when the activation of a molecule has a finite duration, which is generally terminated by reactivation instead of by chemical reaction. If radiation is responsible for the activation, this reasoning cannot be applied without further qualification, but the supposition, introduced below, leaves the mechanism of activation aside and retains its validity, whatever the mechanism of activation may be. We must therefore examine the question how, at constant temperature, owing to the different medium, the number of activated molecules of the reacting substance, can vary within wide limits.

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[1]) R. H. LUECK, J. Amer. Chem. Soc. **44**, 757 (1922).

4. From the value of the specific heat of the molecules, consisting of more than two atoms, as well as from the structure of the absorption spectra, it has been found possible to penetrate farther into the structure of less simple molecules. For the literature [1]) and a summary of the results we may refer to a monograph by V. HENRI, Structure des molécules, Paris 1925. Besides the kinetic energy of the molecule as a whole, a molecule also possesses intra-molecular energy piled up in the vibrations and rotations of the separate atoms with respect to each other, and round definite axes [2]). There is a law of distribution for the energy of a definite vibration or rotation of an atom, as well as for the kinetic energy; for a mean energy of not too small a value we have the law of MAXWELL—BOLTZMANN. For a small value, however, the distribution of energy may strongly diverge from it, since the energy of vibration and rotation changes in quanta.

Now in pretty well every chemical reaction the decomposition of a linkage is a necessary stage, and this fact occurs when the amplitude of the pertinent vibration exceeds a certain critical value, or when the rotation velocity has reached a certain limit. The linkage is broken when the atom or the atomgroup in the case of vibrational energy is, as it were, forced over the limit of rupture, or, in the case of rotational energy, is thrown out by centrifugal force. At a certain temperature the total energy has a certain value, and so is also given the fraction of the whole number of molecules for which the vibrational or rotational energy exceeds such a critical amount (expressed in quanta) that dissociation along this bond must ensue. If therefore, owing to the influence of the medium, or the presence of a catalyst, the reaction velocity does not exclusively depend on the temperature, it stands to reason to hold the medium or the catalyst responsible for an influence on the critical amplitude or rotation velocity. That is to say: forces are exerted by the medium on the molecule which cause a change in the internal coherence of the atomgroups in this molecule.

5. Such forces always exist, except in the case of a rarified gas. As soon as this rarified gas is compressed, and the molecules (all held to be of the same sort) approach each other, commonly the phenomena appear

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[1]) See also Chemical Reviews 4, 189 (1927).

[2]) We do not take into consideration the energy of electrons not present in their lowest orbits.

which find expression in the factor *a* from the equation of state of VAN DER WAALS; when the gas has become a liquid these attractions almost always become so predominating that universally the formation of double molecules and larger complexes must be posited. If the molecules are not all of the same sort these forces can of course cause a much more radical result. Even if the difference in structure of the molecules is restricted to mirror isomerism, the formation of racemic compounds is already possible, while with greater differences the appearance of several compounds, as appears from the melting line, is not at all unusual. Usually the forces which the molecules (*B*) of a medium exercise on an alien molecule (*A*, the substance which takes part in a chemical reaction) need not be of such a nature [1]), that a compound *AB* can separate in the solid state, neither that we need admit the presence of loose complexes in the solution. But without doubt a molecule *A* is subjected to forces of the surrounding molecules *B*, and these forces are not directed on the centre of gravity of the molecule, but on certain atoms of the molecule. The consequence is that a modification takes place in the complex of points and forces which together form *A*, in other words: a deformation of the molecule takes place.

6. Every medium must therefore be considered as a field of force, into which the molecules *A* are brought. This field of force virtually consists of the collective strayfields of the molecules *B*; these molecules exercise outside forces, even when they are chemically saturated. It is a matter of course that, on account of the thermal movement, other parts of molecules enter into each other's fields of force, but among the infinite number of deformations, a certain definite one for every medium, is the most probable. This deformation governs the conduct of *A* as regards the rupture of a certain bond [2]).

For the effect of such a deformation is precisely that for a certain bond in the molecule another number of quanta is necessary to reach the critical value. The atom or the group, united with the rest of the molecule by this bond, may have come, after the deformation, more or less within reach of the other atoms of the molecule. In this case more or fewer quanta are necessary than in the isolated molecule *A* in order to reach the critical amplitude, or in other words: at a certain temperature a greater or a smaller fraction of the molecules are in the critical state which is necessary to render a reaction possible.

7. In complete agreement with what is said above is the behaviour of the compounds, which, by substitution, can more easily split off an atom.

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[1]) The ever recurring heat and volume effects when mixing liquids are consequences of these mutual forces.

[2]) In order to expain catalysis BÖESEKEN has made use of the theory of dislocation of the bonds. For a summary of his theory see: Rec. **45**, 458 (1926) and **46**, 574 (1927).

Acetic acid, dissolved in water, keeps the H atom of the carboxylgroup so securely bound, that for a certain molecule this H atom is not bound only for two or three procent of the time. Substitution in the CH_3 group, which is in the γ position with respect to the H atom, above mentioned, may cause a tendency to dissociation during nearly all the time. By this substitution the forces which keep the H atom bound are much diminished, or the normal amplitude is much increased. Dissolving in different media has also great influence on the ease with which a molecule dissociates, therefore on the forces or amplitudes belonging to the bond of the molecule at that place [1]).

8. Let us inquire a little closer into the influence which the medium undergoes of the dissolved substance. The molecules of the medium are subjected to forces which are equal and opposite to those they exercise themselves. If we start from the pure medium we see that, apart from the bordering layers, there are everywhere present the same number of molecules per unit of volume. The presence of a dissolved substance always causes a change, and this in two different ways. Since, as a rule, the centre of gravity of positive and negative charges in the molecule does not coincide (the molecule will therefore generally have a dipole moment), the substance A will have a directing influence on the molecules of the solvent. But moreover, in the immediate neighbourhood of a molecule A, a greater or smaller quantity of molecules B will be present per unit of volume, depending on the nature of the forces between A and B, than in the medium at places farther removed from molecules A. It is hardly possible to define this precisely for a concrete case, in connection with the intricate actions that manifest themselves. As a rule the last effect will be slight. This cannot be the explanation of the very specific and very pronounced action of the medium which sometimes appears. But it is not our intention to give an explanation of this ; for the moment we want only to study the effect which in the first place is responsible for the influence of pressure. The influence of the medium on the reaction velocity, which in some cases is very great, will not be dominated by the effects of orientation and change of concentration which generally appear, but by operating more strongly on the structure of the molecule, f.i. by the formation of real complexes which can strongly effect the mutual distances and amplitudes of the groups. Pressure, however, will have an influence on this complex, and this influence is connected with the effects above mentioned which now, by the complex itself, will be exercised on the medium.

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[1]) The alteration of the ratio keto-enol by dissolving in different media of f.i. acetylacetic ester shows the change of the preference for a certain structure by deformation, A sensitive reagent on deformation is also the optical rotation as a function of the solvent. to which LANDOLT referred long ago already (Das optische Drehungsvermögen, 2nd ed. Braunschweig 1898. p. 210). We shall revert to this subject again.

9. What can we expect when the medium contains two different sorts of molecules? Let us take a concrete example, and at the same time choose as solute one that possesses very definite properties. We shall take the very thoroughly investigated example of the saponification of bornyl acetate by alkali in an aqueous alcoholic solution, which can serve as the prototype of the whole series of examples which have previously been investigated. The case of bornyl acetate has been studied in different directions, in order to test the predictions based on the views which are developed here, but for the drawing up of these views the results of an investigation about the saponification of the aethylester of o-methoxy-cinnamic acid in a mixture of water and alcohol [1]) could be used. In both cases the solute (the ester) dissolves badly in water, and very well in alcohol. Moreover we can conceive these estermolecules to be constructed of two parts, which behave totally different in respect to the two constituents of the medium. In one case it is the bornylgroup which renders the molecule so sparingly soluble in water, in the other case it is the organic acid function, while the other halves are much less hostile to water. So when a molecule of bornyl acetate is present amidst water and alcoholmolecules, the preference which the bornylhalf of the molecule has for alcohol to water shows itself by a change of concentration of the medium at the place where this half of the molecule is, as compared with the composition of the medium, not in the immediate neighbourhood of the bornylgroup. Just as molecules are directed in the interface of two immiscible solvents, by forces which are exerted on certain parts of the molecule, on the other hand the solute will here cause a partial separation of water and alcohol in the solvent at the place of the bornylgroup, which therefore comes to a change of the relative quantities of the two components on one side of the molecule, with respect to the gross composition of the medium. We can also figure it in this way:

In the solution there are forces between the bornylacetate molecules and the water and alcohol molecules. When too much water is present in the medium the bornylacetate molecules unite into drops; the addition of more alcohol impedes this process. The force between the bornylhalf of a molecule and a watermolecule differs totally from the former and an alcoholmolecule, so that watermolecules are repelled from, and alcohol-molecules are attracted to the bornylhalf. A sufficient quantity of alcohol-molecules only, is able to prevent the bornylacetate molecules, flying the neighbourhood of watermolecules, from attracting each other so strongly that they unite into drops. The distribution of water and alcohol can be modified inversely on the acetylhalf of the estermolecule, or be changed less strongly in the same sense, with regard to the condition of the medium, not in the immediate neighbourhood of the solute. Instead of a medium, possessing in every volume element one and the same proportion of alcohol to water, the medium has now become, by dissolving a substance as bornylacetate, a regular space arrangement of concentration divergencies. If it were possible suddenly to remove all the molecules of the solvent, the condition of complete homogeneous distribution would, by the diffusion process, be reached again after a certain length of time. The force, exercised by the bornylhalf of the molecule on its immediate neighbourhood, which balances the diffusion tendency of the unequally divided water and alcohol molecules, is equal and opposite to the force which this part of the medium exercises on the bornylhalf of the estermolecule. The direction of this force will be equal to that of the strongest fall of concentration, which approximately will agree with the direction of the bond between the two halves of the molecule, which behave totally different with respect to the medium. For the alcoholconcentration will diverge from the gross value especially at the pole of the bornylhalf, where the influence of the other half is least perceptible, while the medium, in the neighbourhood of that pole, has had to collect the greater part of the repulsed water, and to give off the attracted alcohol. When, in the theoretical considerations of DEBIJE and HUECKEL [1]) about a positive ion and its environment, consisting of other positive and negative ions, bornylacetate is taken for the positive ion, water for the other positive ions, and alcohol for the negative ions, we have only to exchange the actions of charges for the repulsions and attractions relating to those molecules, in order to apply their results to this case. The difference is due to the fact that the atmosphere is no longer symmetrical, because the estermolecule consists of two very different parts, and, of course, to the magnitude of the effect, because, instead of free charges dipole moments play a part [2]). The force which is exercised by the medium on the bornylhalf of the molecule, is therefore brought about by the alcoholmolecules, which try to diffuse away, and the watermolecules which have to replace them. The former are attracted, and would have to go from close by to greater distances if they could only obey the inclination to diffusion, the latter are repulsed and are at a great distance. The forces which play a part here quickly decrease with the distance, so that the inclination to bring the solvent again in a homogeneous condition manifests itself in a resultant force, which is directed from the bornylhalf to the medium in the direction mentioned above, of the bond between the two halves of the estermolecule, and which is increased in greater proportion by the more strongly attracted alcoholmolecules, which try to diffuse away, than by the more weakly repulsed watermolecules (farther off) which must, to an *equal amount*, diffuse in that direction.

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[1]) A. L. TH. MOESVELD, Verslagen Kon. Akad. v. Wet. Amsterdam, **32**, 457 (1923); Zeitschr. f. physik. Chemie **105**, 455 (1923).

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[1]) For a synopsis see: Ergebnisse der exakten Naturwissenschaften III, 199 (1924), with an exhaustive list of references; more recent literature in: Ergebnisse der exakten Naturw. VI, 155 (1927).

[2]) These much smaller forces can yet exercise a very great effect, because reaction-velocities are very sensitive for small changes, i.c. small changes in the amplitude of the reacting group.

When the other half of the molecule behaves in the same way with respect to the mixture of water and alcohol as the bornylgroup which we have taken as an example, therefore in a case as benzylbenzoate, we have at the two poles an excess of alcohol and a shortage of water. Then at the two extremities of the molecule forces are at work which are directed towards the medium, and so provide a greater liability to deformation. For an experimental investigation however, it is a drawback that such compounds can be dissolved only in media which are rich in alcohol, and then have a very small velocity of reaction.

If at the other half of the molecule water is the component most in demand, the endeavour to destroy the differences of concentration will, in the same way as has been described for the bornylhalf, give rise to a force which is directed towards the medium. The reasoning is the same, for alcohol we have only to read water, and the reverse.

10. So we see that in a mixed medium, of which the components behave very unequally with respect to the solute, the deformation will be greater than in an unmixed medium, owing to the possibility of partial separation of the components of the medium ; this deformation will be a stretching of the molecule in the direction of the bond which keeps the unequal halves of the molecule together. In the unmixed medium only slight change of concentration takes place by positive or negative condensation of the medium round the solute, or at one of the groups present. This is the reason why the value of the deforming force is limited to a small amount.

A certain separation is also conceivable in the pure solvent. Association is a very universal phenomenon, and the proportion of the different sorts of molecules will probably be other in the neighbourhood of a molecule of the solute than in the free space of the medium. But the contrasts in the behaviour, with respect to the solute, which play such an important part when there is a difference in the components (water and alcohol f.i.) will be not only much slighter with pseudo components, but moreover there will always be an equilibrium adjustment between the simple molecules and the associated complexes. Still a small effect is possible, because the equilibrium constant, valid for the association, may have another value in the free medium than in the neighbourhood of a molecule of the solvent.

In the case of the mixed medium we have still to settle the question : when are the circumstances for deformation most favourable ? This will be the case when the unequality of concentration in the medium and in the neighbourhood of the active group is greatest. If the quantity of one of the components of the medium is just sufficient to keep the ester in solution, the percentage change in concentration, for the same numerical displacement of molecules of water and alcohol per unit of volume, will be a maximum, and upon this depends the tendency to diffuse, as also does the force causing deformation. If f.i. 10 % of water may be present in the alcohol before any separation of the ester begins, and the forces exercised by the bornylhalf on water and alcohol are such that on every 100 molecules 3 molecules of water are replaced by 3 molecules of alcohol in the neighbourhood of the bornylgroup, the proportions of the concentrations which must be balanced by diffusion are $\frac{10-3}{10+3}$ for water, and $\frac{90-3}{90+3}$ for alcohol. Should the medium consist of alcohol of 50 % these proportions would be $\frac{50-3}{50+3}$ resp. $\frac{50-3}{50+3}$ so considerably nearer to 1. The farther the concentration is situated from the critical value, the less "hostile" the medium will behave towards the solute, and the less the proportion of the components need be modified.

11. It might be objected that in our considerations the forces exercised by the molecules on each other must manifest themselves to rather large distances. This is, however, only apparently so, and a consequence of the static picture, given of the solution, and which is not in accordance with the reality. In the case above mentioned of the saponification of 0.01 n. bornyl acetate in a 30 % mixture of alcohol and water the proportion of the numbers of molecules is such, that on an average 12 molecules of water and 6 molecules of alcohol are between 2 molecules of bornyl acetate (reckoned in a straight line to three mutually perpendicular directions). If we imagine this to be a fixed lattice, the changes of concentration, above mentioned, in the immediate neighbourhood of the solute and in the free medium, require forces which make themselves felt along several molecule distances. But taking into consideration the correct kinetic point of view, this signifies that, with the continual motion of the three different kinds of molecules, homogeneous distribution is not formed under the influence of the mutual forces, but that the most probable condition is such, that at the bornylhalf of the solute an atmosphere is found which contains more alcohol and less water than agrees with the gross composition of the medium. This atmosphere moves with the estermolecule, not as one massive whole, but new molecules are assimilated, and old ones are released, while the number that is carried along is subject to fluctuation, and must change when the approach of two estermolecules with the bornylhalves facing each other, requires a greater accumulation of alcohol, so as to prevent a union to a greater complex. When we imagine a layer of the pure medium over the ester solution, the diffusion of the estermolecules, on the basis of the static picture, would not be obvious. In the solution they are so far apart that the resulting power would be practically imperceptible on the molecules which lie on the border of solution and pure medium. If, however, we take into account that all the molecules are in constant motion, it is clear that, only in the direction of

the pure solvent, nothing opposes an unimpeded movement, while in another direction the influence of another estermolecule is always manifested in course of time.

12. From what precedes, we cannot, on the face of it, draw conclusions on the influence of a change of composition of the medium on the velocity of reaction. For, up to now, we have paid attention to the change of only one factor, whereas the change of the medium can have quite other results besides those mentioned. We have not paid attention to the changes which are effected by the medium on the molecules of the other participants of the reaction. But for the problem which is raised here it is of much greater importance to ask ourselves what effect change of pressure will have, all the other conditions remaining unchanged as far as possible. By raising external pressure we approach all the molecules, the consequence of which is a magnifying of all the effects which depend on the mutual forces of the molecules. We shall therefore have to pay special attention to the value of the coefficient of pressure of the velocity of reaction. In the first place we can consider whether the results of our theories are in agreement with the facts known about the magnitude of the coefficient of pressure.

In aqueous solution only the inversion of canesugar [1]), the saponification of aethylacetate [2]), and the reaction between hydrobromic and bromic acid [3]) have been investigated. The saponification of the aethylester of o-methoxycinnamic acid [4]) in a solution of alcohol and water, has been minutely studied, in alcohol of 31 % and of 42.5 %, while of a number of other esters provisional measurements have been made in different, mixed media. Table 1 gives the value of the coefficient of pressure of the velocity of reaction, expressed as the quotient of the velocity at 1500 atmospheres and at ordinary pressure. These figures of course are only approximate in the provisional measurements.

From the figures appears:

1. In the reactions in aqueous medium the influence of pressure is but slight; it may be positive or negative $\left(\frac{K_{1500}}{K_1} > 1, \text{ resp.} < 1\right)$.

2. In all cases the effect is much greater in a mixed medium, and has always been found to be positive. According to the theories developed above this greater effect of pressure depends on the greater chance of deformation in a mixed medium than in a pure medium. If the deformation effect is small other effects can mask it completely.

3. In alcohol of 31 % the coefficient of pressure is considerably greater than in alcohol of 42.5 %. This is also in agreement with the theories

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[1]) ERNST COHEN and R. B. DE BOER, Zeitschr. f. physik. Chemie **84**, 41 (1913); ERNST COHEN and A. M. VALETON, ibid. **92**, 433 (1917).

[2]) ERNST COHEN and H. F. G. KAISER, Zeitschr. f. physik. Chemie **89**, 338 (1915).

[3]) A. L. TH. MOESVELD, Zeitschr. f. physik. Chemie **103**, 486 (1923).

[4]) A. L. TH. MOESVELD, Zeitschr. f. physik. Chemie **105**, 455 (1923).

TABLE I.

A

Reactions	Temp.	Solvent	Influence of pressure $\frac{K_{1500}}{K_1}$
Inversion of canesugar, $^1/_{16}$ n. HCl	25° C.	Water	0.75
„ „ „ $^1/_2$ n. CH_3COOH	25	„	1.05
„ „ „ „ „	35	„	1.06
„ „ „ „ „	45	„	1.09
Saponification of aethylacetate	2.4	„	1.37
Bromic acid and Hydrobromic acid	1	„	0.83
„ „ „ „ „	15	„	0.85
„ „ „ „ „	25	„	0.85
„ „ „ „ „	39	„	0.84
Sap. of aethyl o-methoxycinnamate	25	aethylalcohol of 31%	2.34
„ „ „ „ „	25	„ „ 42½%	2.15

B

Sap. of aethyl o-methoxycinnamate	25	aethylalkohol of 25%	± 2.6
„ „ „ „ „	25	pyridine „ 15 „	„ 2.2
„ „ „ „ „	25	methylalcohol „ 38 „	„ 2.1
„ „ „ „ „	25	aceton „ 28 „	„ 2.8
„ „ „ „ „	25	propylalcohol „ 20 „	„ 2.7
„ „ aethyl o-methoxybenzoate	25	aethylalcohol „ 7 „	„ 2.0
„ „ „ „	25	pyridine „ 2½%	„ 2.4
„ „ aethyl benzoate	25	aethylalcohol „ 18%	„ 2.3
„ „ aethyl anthranilate	25	„ „ 3%	„ 1.9
„ „ benzyl benzoate	25	„ „ 37%	„ 3.0
„ „ linalylacetate	25	„ „ 28%	„ 2.7
„ „ cinnamylcinnamate	25	„ „ 53½%	„ 2.1
„ „ aethyl cinnamate	25	„ „ 28%	„ 2.5
„ „ bornylacetate	25	„ „ 31 „	„ 4.5
„ „ „	25	„ „ 41 „	„ 3.9
„ „ „	25	propylalcohol „ 19 „	„ 4.5
„ „ „	25	pyridine „ 22½%	„ 3.5

The second group (B) refers to provisional measurements; neither has the compressibility been taken into account, which adds about 6% to the figures. These two observations do not apply to the figures of the first group (A).

developed above. The deformation is greatest in the medium which is just capable of keeping the ester in solution.

4. In the cases in which the coefficient of pressure is great enough to study its change with pressure it appears to increase in a pronounced way with increased pressure [1]). The effect of pressure often decreases at higher pressure, as in the case of conductivity, compressibility, etc.; this peculiar fact has already previously been drawn attention to [2]), but no endeavour has been made to find an explanation. We can, however understand it in the scheme, developed above; the closer the molecules are approached, the greater the mutual disturbance. If it should be possible to work far above 1500 atmospheres of pressure, when the molecules strongly oppose further approach, as appears from the continually decreasing compressibility, in other words: when the mutual forces reach very high values, we might expect a formidable increase of the reaction velocity with the pressure. We hope to return to this subject as soon as the new appliances for pressure up to 5000 atmospheres have been installed, and arranged for the measuring of reaction velocities.

13. Now that we have seen that the known facts are in agreement with our views, we can ask ourselves in the second place whether predictions can be made on the basis of the idea formed of the mutual relations of medium and solute. This is indeed the case. The following three possibilities have been passed in review:

1. When in some way or other we can counteract the formation of concentration differences in the mixed medium, this must coincide with a diminution of the coefficient of pressure of the reaction velocity. Now an increase of the temperature will increase the thermal movement of the solvent molecules, and counteract the formation of inequalities in the distribution of water-alcohol. In the same way, the thermal agitation, increasing with the temperature, impedes the orientation of dipoles, which causes the negative temperature coefficient of the dielectric constant. So we shall have to expect that increase of temperature causes a diminution of the coefficient of pressure of the reaction velocity. On account of the increase of temperature the medium is at the same time no longer close to the critical composition, which is just able to keep the ester in solution, at any rate if, as is generally the case, the solubility in the mixed medium increases with the temperature, so that, when retaining the same concentration of ester, the medium can contain, at higher temperature, more of the component with the smaller power of solution.

2. We can try to compensate this last result of increase of temperature by raising the esterconcentration so much that solubility is almost reached

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[1]) Zeitschr. f. physik. Chemie **105**, 466 (1923). The coefficient of pressure is almost twice as great at 1500 atmospheres as at 1 atmosphere in alcohol of 31 %, a little less in alcohol of 42.5%.

[2]) Ibidem p. 470.

again. If we leave the natron concentration unchanged, in order to impart the smallest number of variations at the same time, we can, at increased temperature, compare with each other: *a*. a saponification of equivalent quantities of ester with regard to the natron, which have the same concentrations as at the lower temperature, (which therefore would have to show a smaller coefficient of pressure of the reaction velocity than under the very same circumstances at lower temperature), and *b*. a saponification with surplus of ester with regard to the natron, all other circumstances being equal for the rest, while this surplus can be extended so much, that the medium can just keep all the ester in solution. Then we shall have to expect that in the latter case the coefficient of pressure has become greater again.

This case is very remarkable. We might expect, with the very slight concentrations used here, (in *a*. ester and natron are both 0.01 n., in *b*. 0.016 and 0.01 resp.) that at the same pressure the reaction constants would be the same, calculated by means of equations which hold good for bimolecular reactions, in the case of equivalent and unequal concentrations resp. If therefore a different coefficient of pressure is found here, the values for the reaction constants, in both cases, do not run parallel with the pressure, and we have here an autocatalytic effect, which increases with pressure, and is already clearly perceptible in such slight concentrations.

3. Finally, instead of surplus of ester, we can add another substance, which in a similar way can effect a partial separation of the medium, as f.i. borneol. Every borneolmolecule will try to envelop itself with an atmosphere which is relatively richer in alcohol than the medium; for the bornylacetate molecules a medium then remains which has become already poorer in alcohol. So the ester is as it were dissolved in a medium which lies closer to the critical composition, and can therefore cause a greater deformation of the ester. When therefore, at increased temperature, we add to the equivalent mixture of ester and natron so much borneol, that the latter can just be kept in solution, the coefficient of pressure must in this case be found greater than when borneol is not added, all the circumstances, and also the temperature, being the same for the rest. In this case borneol must play the part of a catalyst which increases in activity with increasing pressure. These three predictions have all been tested by experiment in the case of the saponification of bornylacetate by natron, in alcohol of 30 %, and in the three cases the expected effects have been found to amounts far exceeding the errors of experiment. In another paper we hope to enlarge upon the experimental particulars.

14. Whether the mechanism of activation depends on collision, or radiation, or on both, need not be considered here. The deformation, brought about by the medium, modifies the mean amplitude of the vibration or the rotation velocity of that part of the molecule which plays a part in the reaction. The number of molecules in which these magnitudes surpass

a certain critical value is different too and this number is proportional to the reaction velocity. The maintaining of the exact fraction of activated molecules can take place in the same way as before the deformation.

The explanation of the change of the reaction velocity by pressure does not rest upon particular suppositions about the mechanism of activation as this might be changed by pressure. It would indeed be difficult to connect in this way the increase of the reaction velocity at 1500 atmospheres to 4 × the value which holds good for one atmosphere, with the increase of the number of collisions, or of the acitivating radiations at the change of volume which then appears, and which amounts to only ± 6 %. Here, too, the effect must be attributed to the change of amplitude, or of the rotation velocity, when by external pressure the molecules are approached and exercise greater forces on each other. Collisions have of course another effect on a deformed molecule, while other quanta of radiating energy can, under the modified circumstances, also bring the molecule in the activated condition.

15. When the non reacting molecule does not undergo a change itself, but only after the formation of intermediate products, the above considerations must of course be applied to this complex, and not to the single molecule, which reacts according to the reaction equation. But actually there is only a gradual difference between an intermediate product of definite chemical composition and a molecule which is endowed with a definite atmosphere, which plays the part of a loose complex, that is to say: with respect to the influence of pressure on the reaction velocity, of course not when, in totally different media, also as regards the components, we may expect totally differently composed intermediate products. See also the concluding part of § 8.

16. Finally we might put the question whether a similar reaction, as we have taken as an example could not show a drift in the reaction constant, if the reaction is studied along a great interval of concentration. For, during the reaction, the ester concentration diminishes continually, so that the medium gets less close to the critical composition, with respect to the quantity of ester which is still present. In connection with prediction 3 this is to a large extent compensated by the reaction product which is formed out of the ester, containing the group which behaves in a totally different way with respect to the two components of the medium. Previously it has been observed already [1]) that with similar reactions a small drift can play a part, though then it was attributed to an incomplete equivalence of ester and natron (in connection with the electrolytic dissociation in the medium used). At this moment it is not quite possible to settle, whether one of these effects, or both, are responsible for this slight drift. In this investigation the drift has been eliminated by a slight

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[1]) Zeitschr. f. physik. Chemie **105**, 455 (1923), see p. 461.

change of the ester concentration, as was also done previously. For further particulars we refer to a later communication.

SUMMARY.

In order to explain the facts known about the influence of pressure on the reaction velocity, we have passed under review the condition of dissolved substances in simple and in mixed media. The existing experimental material allows of the development of an effectual conception.

This conception is based on the supposition of a partial separation of the components of the medium, which is caused by the molecules of the dissolved substance, provided that it satisfies some definite conditions. This is attended with a deformation of the molecule of the dissolved substance.

In consequence of these views three predictions have been elaborated about the influence of changes of temperature and catalysts on the value of the coefficient of pressure of the reaction velocity, which are justified by the experiment.

Utrecht, September 1927. VAN 'T HOFF-*Laboratory.*

Physics. — *On the rectilinear diameter of ethylene*. By E. MATHIAS, C. A. CROMMELIN and H. GARFIT WATTS. (Communication N⁰. 189*a* from the Physical Laboratory at Leiden.) (Communicated by Prof. W. H. KEESOM.)

(Communicated at the meeting of November 26, 1927).

§ 1. The density curve and the rectilinear diameter of ethylene we thought would be an interesting subject for investigation, firstly because the results that have so far been obtained are only of a temporary character [1]) and secondly because this substance is one of those used in refrigeration. The present research forms part of a series of observations upon the diameter of oxygen [2]), argon [3]), nitrogen [4]), hydrogen [5]), neon [6]) and helium [7]). All these investigations were carried out in the Physical Laboratory of the University of Leiden.

§ 2. Our apparatus was almost exactly the same as that used in the above mentioned investigations, for particulars we may therefore refer to the papers already published on these. The only difference is that as liquid in the cryostat we used ethyl-chloride for temperatures above —24° C., methyl chloride for temperatures between —24° C. and —103° C. and ethylene for those below —103° C. Temperatures above the freezing-point of mercury were measured with a mercury thermometer standardized in the Physikalisch-Technische Reichsanstalt at Charlottenburg ; those that were lower, by means of a platinum resistance thermometer compared directly with the helium thermometer.

The ethylene was first technically prepared (ethyl-alcohol and sulphuric acid) and afterwards purified as thoroughly as possible by means of repeated distillation at a low temperature.

For the weight of 1 liter under normal conditions we took the figure 1.2609_8 [8]).

In the following table we have arranged the values found for the densities δ and δ' for the liquid and the saturated vapour at the same temperature θ and for the ordinates of the diameter.

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[1]) L. CAILLETET and E. MATHIAS, Journ. de Phys. (2) **5** (1886) p. 549.

[2]) C. R. January 1911. Leiden Comm. N⁰. 117.

[3]) C. R. 13 January 1913. Leiden Comm. N⁰. 131*a*.

[4]) C. R. **160** (1915) p. 237. Leiden Comm. N⁰. 145*c*.

[5]) C. R. **172** (1921) p. 261. Leiden Comm. N⁰. 154*b*.

[6]) C. R. 20 November 1922. Leiden Comm. N⁰. 162*b*.

[7]) C. R. **180** (1925) p. 1005. Leiden Comm. N⁰. 172*b*.

[8]) Determined by STAHRFOSS in the laboratory of PH. A. GUYE at Geneva. See Arch. d. Sc. physiques et naturelles, Genève 28 (1909), p. 384.

θ	δ (observed)	δ' (observed)	y (observed)	y (obs.) — y (calc.)	y (obs.) — y (calc.) in %
+ 7°.98C.	0.28726	0.15268	0.21997	+0.00307	+ 1.40
+ 6.50	30342	13716	22029	+ 00249	+ 1.30
+ 5.84	30840	13266	22053	+ 00232	+ 1.05
— 7.70	37721	076050	22663	+ 00013	+ 0.06
— 10.93	38818	067215	22770	— 00078	— 0.34
— 14.18	39855	059942	22925	— 00123	— 0.54
— 19.20^5	41313	051138	23214	— 00141	— 0.61
— 24.33	42655	041854	23420	— 00250	— 1.07
— 37.13	45610	029465	24279	— 00175	— 0.72
— 48.15	47822	020407	24932	— 00197	— 0.79
— 63.41	50588	012584	25923	— 00141	— 0.54
—103.01	56740	0021928 1)	28480	— 00011	— 0.04
—114.69	58380	0011127 1)	29246	+ 00040	+ 0.14
—129.90	60449	00037586 1)	30244	+ 00106	+ 0.35
—145.07	62465	00009363 1)	31237	+ 00169	+ 0.56

The values calculated for the ordinates of the diameter, deduced from the observations according to the method of the least squares are represented by the formula

$$y = 0.22179 - 0.00061277\,\theta .$$

The direction constant of the diameter is therefore

$$a = -\,0.00061277.$$

(differs very little from that of methane).

The formula for the diameter gives +9°.5 C. 2), at the critical temperature, for the critical density

$$\triangle = 0.21597$$

The critical coefficient is

$$\frac{R\,T_k}{p_k\,v_k} = 3.524$$

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1) Calculated by means of the general reduced equation of state. Comm. Leiden Suppl. N⁰. 19.

2) E. Cardoso and E. Arni, Journ. de chimie physique **10** (1912) p. 504.

(T_k = critical temperature, p_k = critical pressure, v_k = critical volume and R = gas constant).

§ 4. The deviations of the diameter are not so small as in hydrogen and neon, they are sometimes even greater than 1/100; nevertheless ethylene may be said to conform approximately to the laws of the rectilinear diameter. The deviations are of the same systematic character that we have met with in other substances, such as argon and carbonic acid, i.e. in the neighbourhood of the critical point the diameter is slightly concave towards the temperature axis, while at low temperatures it is convex¹).

This research was carried out with the aid of a grant from the Caisse de recherches, which the Académie des Sciences in Paris extended to us, for which we render our sincere thanks.

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¹) See Comm. Leiden Suppl. N⁰. 23, Enc. Math. Wiss. V. 10, § 85 *a* and *c*; further § 50 note 576.

Physics. — *Vapour tensions of liquid ethylene.* By C. A. CROMMELIN and H. GARFIT WATTS. (Communication N⁰. 189*b* from the Physical Laboratory at Leiden.) (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of November 26, 1927).

§ 1. *Introduction.* The critical pressure and temperature of ethylene have been measured by CARDOSO and ARNI [1]) (50.65 atm. and 9°.50 C. respectively); vapour pressures between —103° and —150° C. were determined by HENNING and STOCK [2]) with an accuracy of 0.1 mm. But between the critical point and boiling point so far only VILLARD's [3]) figures were known, which did not give a greater accuracy than 0.1 atm. The determination of the densities of the liquid and of the saturated vapour [4]) furnished the opportunity (while also rendering it essential) for making a new series of determinations of vapour pressure, the results of which are given in this paper.

§ 2. *Apparatus.* Pressures above 20 atm. were measured with the closed hydrogen manometer [5]), those above 20 atm. with an open standard manometer [6]). The ethylene was compressed and liquefied in a small reservoir provided with an electro-magnetic stirrer.

Measurements above —20° C. were made in a bath of liquid ethyl-chloride, those below this temperature in a bath of liquid methyl-chloride. The temperatures of the ethyl-chloride were determined by means of two mercury thermometers, those of the methyl-chloride by two platinum resistance thermometers.

§ 3. *Purity of the ethylene.* Our ethylene was prepared from alcohol and sulphuric acid; it was then lead through a spiral cooled in solid carbonic acid and alcohol (± —90° C.) and finally solidified in a glass bulb plunged in liquid air, after which the volatile impurities (e.g. air) were very thoroughly expelled with a diffusion pump; after partial heating the middle portion was pumped off, the less volatile constituents remained behind in the last fraction. This treatment was repeated three times. The gas thus purified was then compressed in a small steel cylinder.

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[1]) E. CARDOSO and E. ARNI, Journ. de chim. phys. **10** (1912) p. 504.

[2]) F. HENNING and A. STOCK, Zeitschr. f. Phys. **4** (1921) p. 226.

[3]) P. VILLARD, Ann. d. Chim. et de Phys. (7) **10** (1897) p. 387.

[4]) E. MATHIAS, C. A. CROMMELIN and H. GARFIT WATTS, These Proceedings. p. 1054, Comm. Leiden N⁰. 189*a*.

[5]) Comm. Leiden, Nos 78, 97, 118, etc.

[6]) Comm. Leiden, Nos 44 and 146.

§ 4. *Accuracy.* The mercury thermometers were standardized in the Physikalisch-Technische Reichsanstalt within an accuracy of 0.01 degree; the platinum thermometers were compared with the helium thermometer within an accuracy of 1/50 degrees. At points 6, 7 and 9 the difference in indication of the two platinum thermometers was less than 0.01 degrees, at points 8 and 10 this difference was 0.03 degrees. The accuracy of the pressure measurements may be taken at about 1/4000.

§ 5. *The results* are given in the table below. The temperatures are given in Kelvin degrees on the Celsius scale, and on the absolute scale, where —273°.09 C. is taken as the absolute zero. The pressures are given in international atmospheres (1 int. atm. = 75.9529 local cm at Leiden).

N⁰.	θ	T	p (int. atm.)
1	+ 7°.90 C.	280°.99 K.	48.162
2	0.00	273.09	40.276
3	— 7.54	265.55	33.923
4	—10.01	263.08	31.971
5	—20.01	253.08	24.905
6	—30.53	242.56	18.851
7	—41.01	232.08	13.907
8	—52.09	221.00	9.774
9	—60.90	212.19	7.206
10	—69.27	203.82	5.259

Physics. — *Preliminary isotherms of ethylene*. By C. A. CROMMELIN and H. GARFIT WATTS. (Communication N⁰. 189c from the Physical Laboratory at Leiden.) (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of November 26, 1927).

§ 1. Isotherms of ethylene have been measured by AMAGAT[1] at 0°, +20° and +70° C. and by MASSON and DOLLEY[2] at +24°.95 C. While measuring the diameter of ethylene we took the opportunity for determining a few isotherms as well. Although the ground covered is not large, our measurements were useful for calculating approximate values for B and C in the empirical equation of state of KAMERLINGH ONNES, so that we think it worth while to publish our results.

§ 2. For a description of the method and apparatus used we refer to the numerous earlier communications from the Physical Laboratory at Leiden regarding isotherm determinations; for the purification and for the temperature measurements at these comparatively high temperatures, to the paper in these Proceedings on the diameter and vapour pressure of ethylene.

§ 3. The results of our measurements are given in table I. The temperature is reduced on the thermodynamic scale; pressure is given in international atmospheres.

§ 4. *Virial coefficients.* We have endeavoured to represent our observations by KAMERLINGH ONNES's empirical equation of state

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} + \dots$$

in which the coefficients D_A etc. could be taken as 0, as the 4th and following terms only come into play at greater densities. Considering the small number of observations and the temporary character of our calculations, it was not worth while to apply the method of least squares. The curve that corresponds to the equation was simply drawn through two suitably choosen points; in some cases it was afterwards made more complete by a small variation in the coefficient.

In table II the results of these calculations are combined, while coefficients

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[1] E. H. AMAGAT, Ann. de chimie et de phys. (6), **29**, June et Augustus 1893.

[2] I. MASSON and L. G. F. DOLLEY, Proc. R. S. (A) **103** (1923) p. 524.

TABLE I.
Isotherms aethylene.

Serie	N⁰.	θ	p intern. atm.	d_A	v_A	pv_A (obs.)	pv_A obs.—calc.
IV	1	+20°.18C.	23.021	25.385	0.039393	0.90687	—0.00030
	2		26.150	29.704	33665	88034	+ 35
	3		30.715	36.638	27294	83833	+ 34
	4a		38.339	50.360	19857	76130	+ 60
I	1	+10.17	23.008	26.946	0.037111	0.85387	+0.00110
	2		25.983	31.553	31693	82347	+ 26
	3		29.614	37.605	26592	78751	+ 163
	4		36.754	52.392	19087	70152	— 34
V	1	+ 0.10	21.951	27.036	0.036989	0.81194	—0.00011
	2		24.789	31.765	31481	78039	0
	3		27.128	36.071	27723	75208	— 6
	4		30.289	42.649	23447	71020	0
	5		34.127	52.323	19112	65223	+ 101
II	1	— 1.36	21.947	27.460	0.036417	0.79925	—0.00098
	2		25.127	32.895	30400	76385	0
	3		28.611	39.740	25164	71997	+ 16
	4		33.687	52.302	19120	64409	0

according to AMAGAT's isotherms are added, borrowed from earlier calculations by KAMERLINGH ONNES, which have not been published before.

TABLE II.

θ	A_A	$B_A \times 10^3$	$C_A \times 10^6$	
+70° C.	+1.2657	—5.8507	+16.064	AMAGAT
+20.18	1.0825	7.4319	20.700	C. A. C. and H. G. W.
+20	1.0812	7.3756	21.880	AMAGAT
+10.17	1.0455	7.7831	23.350	C. A. C. and H. G. W.
+ 0.10	1.0084	7.7198	17.083	" " "
0.00	1.0080	8.5354	30.936	AMAGAT
— 1.36	1.0030	7.9604	21.002	C. A. C. and H. G. W.

The values of A_A are calculated from those of A_{A_0} by the formula $A_A = A_{A_0}(1+\alpha t)$, in which for α the value 0.0036618 is assumed. As it is calculated, B_A and C_A can now be represented as functions of the temperature by a polynomium. The observation material, however, is not large enough for it to be worth while making rather elaborate calculations about it, so that we have preferred to smooth out the coefficients graphically. The results of this smoothing will be found in table III.

TABLE III.

θ	$B_A \times 10^3$	$C_A \times 10^6$
+70° C.	−5.8	$+16^5$
60	6.1	17
50	6.3	17^5
40	6.5^5	18
30	6.9	18^5
20	7.2	19^5
10	7.6	21
0	8.0	22^5

§ 5. As far as it was possible from the graphic representations, we could determine that our isotherms were in good agreement with those of AMAGAT. Those of MASSON and DOLLEY deviate completely from ours. In the $\frac{pv_A}{T}$, d_A-diagram all isotherms should meet the $\frac{pv_A}{T}$ axis in one point; AMAGAT's and ours fulfil this requirement, MASSON and DOLLEY's do not in the least. We have not been able to discover any explanation of this irregularity.

Microbiology.— *On differential filtration* [1]). By A. PIJPER.

(Communicated at the meeting of December 17, 1927).

The dimensions of bacteria, as given in textbooks, are unsatisfactory. Such statements are not only too vague, as for instance when a bacillus is said to be 0.5 to 1 micron thick, but the different authors also often contradict one another. Thus it seems to be quite unsettled whether for instance b. typhosus is thicker than b. coli or whether the reverse is true.

This condition of affairs becomes comprehensible when one realizes that these determinations of size are performed by means of eye-piece micrometers, on material of varying origin, and usually including a small number of individuals only, and that therefore the "measurements" obviously are mere approximations.

A more exact knowledge of the relative sizes of bacteria seems to me to be of sufficient importance, theoretically and practically, to merit calling attention to measurements which can be performed by the diffraction-method as indicated by me [2, 3, 4]). The results of these measurements throw new light on certain unexplained phenomena, and point the way towards a new method for isolating bacteria, which method I have designated differential filtration.

The diffraction-method makes use of the fact that many kinds of bacteria in surface-cultures show such a regular arrangement of the individual microbes that the culture can be employed as a diffraction grating. In the case of staphylococci their spherical shape readily explains this. In a staphylococcal surfaceculture consisting of two layers of bacteria, these two layers will naturally fit themselves together in such a way that small apertures will be left open between the cocci, and these small apertures will be situated on straight lines intersecting at angles of 60°. Small variations in the size of individual cocci here and there will cause these lines to wheel about as compared with the lines at other spots. Such a culture may therefore be regarded as a grating with equidistant lines running in all possible directions. The distance between the lines is a function of the thickness of the cocci. Under suitable conditions therefore staphylococcal cultures will produce circular spectrums, the size of which is a function of the thickness of the cocci. A further consideration of the physical aspects of the matter would take up too much space. It is quite feasible to produce, with the aid of staphylococcal cultures, beautiful and bright spectrums with diameters of several centimeters. The diameter of a given coloured circle can be recorded directly by suitable means, or can be registered by means of a colourphotograph. In either case an accuracy of at least one millimeter can be achieved.

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[1]) Part of the apparatus used in these experiments was procured through the kind assistance of the Research Grant Board of the Union of South Africa.

[2]) The Med. Journal of S. Africa, August, 1918.

[3]) S. African Medical Record, June, 1923.

[4]) S. African Medical Record, June, 1925; October, 1925.

Apart from staphylococci I have also found the method applicable to bacteria of the coli-typhoid group. This suggests that in surface cultures of these bacilli, the individuals stand upright, at right angles to the surface of the culture, because otherwise the regular pattern necessary for its proper function as a diffraction-grating, could not be obtained. Considerations of a mechanical nature support this assumption. The thickness of the bacilli then plays the same part as the diameter of the cocci, and determine the dimensions of the spectrums.

This is, briefly, the diffraction-method of measurement. Constant results can only be expected if one scrupulously adheres to an established technique, both as regards the preparation of mediums and the planting out of cultures. The most disturbing factor is desiccation, to which the size of bacteria has proved to be most sensitive, and surface-cultures naturally are much subject to desiccation. Old and thick cultures therefore are unsuitable.

Working on these lines I have succeeded in establishing the sizes of the spectrums which belong to given kinds of bacteria, and in calculating values therefrom for the mean relative thickness of these bacteria. The relation between the size of the elements of the grating and the thickness of the bacteria may be regarded as constant. The thickness of the bacteria however here includes the ektoplasm, of which little is known. It therefore at this time seems better not to attempt to give absolute values for the thickness of the bacteria, but to use the thickness of b. typhosus as the unit measurement. The b. typhosus was chosen because this bacterium exhibits such a remarkably small range of variation in its other characters. It may be added that the results of the diffraction-measurements otherwise compare very well with the accepted dimensions of bacteria, as all calculated values lie in the neighbourhood of 1 micron.

In this way I found, that, expressed in b. typhosus units, b. coli Escherich had a thickness of 1.11, b. cloacae of 1.08, b. neapolitanus of 1.15, b. lactis aerogenes of 1.38, and various not further classifiable representatives of the group of about 1.3. In every instance more than one strain of bacilli was examined, and of typhoid bacilli more than twelve strains were measured. A single strain of paratyphoid-B bacilli measured 0.98 and a single strain of b. pyocyaneus 0.88.

Similarly it was found that staphylococci from a carbuncle had a thickness of 1.08 b. typhosus units, and various cocci from furuncles of 1.11, whilst white staphylococci were 1.3 thick, and staphylococci from air reached 1.6.

Very young cultures often seemed to contain thicker bacteria than older cultures. This initial stage was followed by a period of several hours during which constant values were recorded, and after that the bacteria steadily became thinner. For this terminal change the unavoidable desiccation must be held responsible. The initial, and perhaps only apparent, increased size may perhaps be due to the scantiness of growth in the early stage, when the grating may still consist of one layer of bacteria only, which produces an entirely different type of grating. Perhaps also we are here dealing with the phenomenon described by others on the strength of microscope-measurements, viz., that young individuals in fresh cultures show enlarged sizes [1]).

The diffraction-method thus demonstrated that certain bacteria under given conditions, amongst which a sufficient degree of humidity appears supreme, show constant differences in thickness, and that generally speaking the thickness stands in inverse relation to the pathogenicity.

The idea now suggested itself that the discovered differences in thickness might throw some light on well-known but unexplained phenomena, and that perhaps some practical application might be found.

FRIEDBERGER's experiments on the ascent of bacteria have remained unexplained. FRIEDBERGER dipped strips of filterpaper into fluids containing mixed suspensions of bacteria, and noticed, by placing these strips after a few minutes on solid media, that some kinds of bacteria ascended higher into the filterpaper than others, or as I would prefer to put it, that some kinds of bacteria were carried to greater heights on the ascending current of fluid than others. Attempts at explanation have failed, motility was proved to play no part, and the conception of adsorbability brought no light. The matter becomes very simple when one remembers that it is extremely probable that the thinner bacteria find it easier to pick their way between the obstructing fibres of the filterpaper when carried upwards by the current. As a matter of fact it appears from FRIEDBERGER's reports that those bacteria which ascend highest, prove to be the thinnest when measured by the diffraction-method. The order in which FRIEDBERGER places bacteria according to their powers of ascent, corresponds with the order in which they have to be placed according to their thickness. FRIEDBERGER is inclined to accept this explanation [2]), although he omits to mention this new principle in his recent communication on the subject, in which he describes an application of the filterpaper-method to the purification of vaccine lymph from contaminating staphylococci [3]). Miss SLUITER, who performed experiments on the ascent of red blood cells, admits the possibility that the size of the cells plays a part [4]).

From this perfectly natural explanation of the ascent of bacteria in filterpaper, it is only a small step to the explanation of certain experiments on filtration, which also stand in need of elucidation. CARNOT and GARNIER ¹), and later CARNOT and WEIL—HALLE ²), have claimed, and this has later been partly confirmed by PLANTENGA ³), that when mixed suspensions of bacteria, containing typhoid bacilli, are brought into one limb of a *U*-tube, which is filled with broth, and contains sand at the bend, the typhoid bacilli will be the first to appear in the other limb, leaving behind the other bacteria. The explanation was sought in the greater motility of the typhoid bacilli, and the French authors speak of "auto-sélection par motilité". FETSCHER's method which pursues the same object and according to FETSCHER is based on the same principle, replaces the sand by a woollen thread ⁴).

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[1]) HENRICI, Science, Vol. **61**, 1925.

[2]) Private communication.

[3]) Deutsche Med. Woch. 1927.

[4]) These Proceedings, Vol. **28**, 1925.

Both methods were extensively tried by me. The results up to a point agree with the inventors claims, but they at the same time have confirmed my contention that the motility does not play the part ascribed to it, and that here also differences in thickness afford a better basis for explanation. When non-motile bacteria are used, such as staphylococci, the experiments succeed just as well, and it is always that bacterium which comes through first which by the diffraction-method was found to be the thinnest.

As all these methods for the isolation of bacteria are obviously dependent on an identical principle, viz., that thinner bacteria more easily find their way through narrow paths, it seems justified to speak in all these cases of differential filtration. Whether the driving force has to be looked for in active growth, diffusion, currents generated by heat, or motility, to my mind seems to be without importance for the explanation of the phenomena.

It proved very difficult to procure sterile sand in sufficient quantity. FETSCHER's apparatus is expensive and fragile. The experiments therefore were continued with cotton wool as filter-material. In a test tube a glass tube was placed, about half as wide as the test tube, and three quarters of its length. This inner tube was bevelled at its lower end, and a rim at its upper end prevented too close contact with the outer(-test)tube. A fairly tight plug of cotton wool, about 2.5 centimeters long, was pushed into the inner tube up to a distance of about 2.5 centimeters from its lower end. Fluid, usually broth, was then poured in, to a level a couple of centimeters over the upper end of the cotton wool plug, and the whole apparatus was sterilized in the usual way. If now bacteria were brought into the upper end of the inner tube, over the cotton wool plug, then these bacteria after a time found their way through the cotton wool and appeared in the outer tube. With this kind of apparatus a large number of filtration experiments were performed. Mixtures of bacteria in varying concentrations

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¹) C. R. Soc. Biol., 21 juin et 5 juillet 1902.

²) C. R. Acad. Sc., T. 160, N⁰. 4, 25 janvier 1915.

³) Ned. T. v. Geneesk., 1925.

⁴) Mediz. Klinik, 1926, N⁰. 35.

and quantities were inoculated into the inner tube, and with intervals of 12 hours the contents of inner and outer tubes were plated and examined. In seven instances a few platinumloopfuls of a mixture of equal parts pathogenic and non-pathogenic staphylococci were brought into the inner tube. The fluid used was ordinary broth, and control tests showed that these bacteria endured one another's presence quite well for many days. The thickness of the staphylococci used in the different experiments varied from 1.08 to 1.2 b. typhosus units for the pathogenic cocci, and from 1.3 to 1.6 units for the non-pathogenic ones. In six out of the seven instances a pure culture of the pathogenic staphylococci was found in the outer tube after due waiting, the seventh time a few non-pathogenic cocci had also passed through, but they were a small minority.

Similar experiments with typhoid bacilli combined with staphylococci yielded four times out of four experiments the result that a pure culture of typhoid bacilli made its appearance in the outer tube, and it was immaterial whether pathogenic or non-pathogenic cocci were used.

Inoculations of a mixture of micrococcus abortus and a pathogenic staphylococcus did not produce the expected result as long as the fluid employed was broth. It was expected that the micrococcus abortus, which is very much smaller than any staphylococcus, would filter through first. From control platings from the inner tube however it became clear that the antagonism between micrococcus abortus and staphylococci was so pronounced that after a very few hours no living micrococcus could be detected in the inner tube. When now the broth was replaced by saline. then the results were quite different, and twice out of two experiments the micrococcus got through first in pure culture. Of course there was no multiplication of the germs in the saline, and this rendered it comprehensible that the results were delayed several days.

It may justly be stated that these experiments with non-motile bacteria, fully confirmed the assumption that the thickness of the bacteria is the decisive factor.

A mixture of typhoid bacilli and (non-motile) b. lactis aerogenes inoculated into the inner tube, gave 30 times out of 33 attempts the result that in the outer tube a pure culture of typhoid bacilli appeared. In the remaining three instances the typhoid bacilli were in the majority in the outer tube, and it seems likely that if only the plating had been done somewhat earlier, the success would have been complete in these instances as well. Now the difference in thickness between typhoid bacilli and b. lactis aerogenes is very marked, viz. 1 as against 1.38. That this difference in size is the decisive factor and not, as might be suggested, the difference in motility, was demonstrated by further experiments in which so much typhoid serum was added to the tubes that the typhoid bacilli quite lost their motiliy. The results of the filtration were unchanged, both in broth and in saline.

Typhoid bacilli and b. lactis aerogenes exhibit no antagonism and this facilitated the experiments. Between b. typhosus and b. cloacae the antagonism was found to be so marked that at first it appeared impossible to keep typhoid bacilli alive at all in a mixture of these two bacteria. Their difference in thickness is but small, viz. 1 as against 1.08, which initially threatened to endanger successful differential filtration of b. typhosus. Replacing all sugar in the broth by phosphates did not improve the conditions for b. typhosus. Addition of malachitegreen, caffein, crystal-violet, did not have the desired result. Similarly the mediums of SACQUEPÉE ¹), of NISZLE ²), of WADE, KELLY and GIBLIN ³), of FETSCHER ⁴), all devised to favour the growth of b. typhosus and keep other bacteria in check, did not succeed in keeping b. cloacae back so that b. typhosus could be kept alive. In the end it was found that only the medium described by WILSON and BLAIR ⁵) (on 100 cc. broth 5 cc. of a 20 % glucose solution, 2.5 cc. of a 20 % sodiumsulphite solution, and 2 cc. liquor bismuthi B. P.) was able to show live typhoid bacilli 12 hours after inoculation with equal quantities of b. typhosus and b. cloacae. If ten times more b. cloacae than b. typhosus were introduced, then after 12 hours no living typhoid bacilli could be found.

Filtration experiments with this medium succeeded quite well. In 18 out of 21 attempts the outer tube showed a pure culture of typhoid bacilli after 12 hours. In some instances markedly fewer typhoid bacilli than b. cloacae had been inoculated into the inner tube, sometimes the proportion was 1 : 1000, or 1 : 10.000, in one case even 1 : 1.000.000. Even then pure cultures of typhoid bacilli were found in the outer tube. In one experiment where the proportion was 1 : 100.000, chiefly typhoid bacilli were found in the outer tube with a slight admixture of b. cloacae. These results of differential filtration are, apart from the slight difference in thickness of the bacilli, all the more remarkable because this strain of b. cloacae was at least as motile as b. typhosus.

Good results were also achieved in the differential filtration of typhoid bacilli versus b. coli ESCHERICH. The antagonism which in this case appeared in broth, could be kept in check by making the filtration take place in brilliantgreenpeptone water. In seven out of eight attempts a pure culture of typhoid bacilli was found in the outer tube, and the eighth time a few colonies of b. coli appeared, together with numerous colonies of b. typhosus. It made no difference whether equal parts of b. coli and b. typhosus or one part b. typhosus against one hundred parts b. coli were placed in the inner tube.

Still further differential filtration experiments were performed with 24 representatives of the coli-typhoid group, which all had been found

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¹) Bulletin Inst. Pasteur, 30 Sept. 1926, N⁰. 18.

²) Centralbl. f. Bakt., July 21, 1927.

³) Centralbl. f. Bakt., Aug. 10, 1926.

⁴) l. c.

⁵) Journal of Pathol. and Bact., July 1927, Vol. 29, N⁰. 3.

thicker than b. typhosus by the diffraction-method. As a rule the bacilli varied so much from known forms in their biochemical reactions that no names could be given to them. In half of the cases it appeared that their antagonism to b. typhosus was so strong that typhoid bacilli could not be kept alive together with them in any medium, even for a few hours. With the remaining twelve, differential filtration against typhoid bacilli was attempted, sometimes in brillantgreenpeptonewater, sometimes in WILSON and BLAIR's medium, and in eleven out of the twelve instances a pure culture of typhoid bacilli appeared in the outer tube.

SUMMARY.

The relative thickness of staphylococci and of bacilli of the coli-typhoid group can be determined by the diffraction-method of measurement described.

The thickness of these bacteria remains constant under suitable conditions.

Generally speaking, pathogenic representatives of the two groups are thinner than non-pathogenic ones.

The explanation of FRIEDBERGER's filterpaper-ascent experiments and of so-called sandfiltration of b. typhosus must be sought in differences in thickness of the bacteria concerned, and not in differences in motility.

A technique is described which, by filtration through cotton wool, allows the separation of thinner microbes from thicker ones, and this is called differential filtration.

As b. typhosus is a particularly thin bacillus, differential filtration often succeeds in separating b. typhosus from other bacteria. Where it fails to do so, the failure is usually due to the antagonism of the bacteria concerned, which has the effect of killing the typhoid bacilli before differential filtration can take place. In some instances a suitable filtration medium can counteract this antagonism, but a medium which suits all cases has not been found.

Pretoria, October 1927.

Chemistry. — *On the Accurate Measurement of the Specific Heat of Solid Substances between 0° and 1625° C.* **II.** *The Specific Heat of Platinum and Tungsten.* By Prof. Dr. F. M. JAEGER and Dr. E. ROSENBOHM.

(Communicated at the meeting of October 29, 1927).

§ 1. As first results obtained in the measurements made by the method described in our previous paper [1]), we communicate in the following pages the data acquired in the case of the metals *platinum* and *tungsten*.

In the first place the specific heat of pure *platinum* was determined. The material used consisted of the purest platinum exempt of iridium, as used by HERAEUS for thermo-couples and resistance-thermometers. A crucible K (see the previous paper Fig. 6) made of this metal, was closed by a cover furnished with a small hooklet h; moreover, a small tube m was fixed in this cover for placing the junction of the thermo-couple in it in such a way, that this junction stood in the centre of the crucible. The latter was filled out with ten or twelve little spheres of the same metal, the total weight of the platinum thus being about 52.7 grammes. The vessel was suspended in the space of the furnace where this has no appreciable temperature-gradient by means of an iridium-free platinum-wire d and heated to the desired temperature. When the temperature had remained constant during a long time, the platinum-wire d was at its lower end suddenly melted through by the aid of a strong electric current passing through it, which current was introduced the contacts z and the strong (2 mm.) platinum-wires x. The thus detached crucible passed the MARQUARDT-tube GG' and was caught in the calorimeter. When the measurement was made, the weight of the crucible was every time redetermined, because the melting of the wire d eventually caused some liquid platinum to fall on the cover and because, moreover, at very high temperatures there is always some danger of a diminuition of the weight of the crucible by a slight volatilization of the metal in presence of the oxygen of the air. The results are collected in the following table I and compared with those obtained by WHITE [2]), who worked with another material and also used another kind of apparatus (a liquid-containing calorimeter). The values of $\overline{c_p}$ necessary for the comparison are calculated by means of WHITE's formula: $\overline{c_p} = 0.03175 + 0.0000032\ t$. From our measurements the values Q were derived, representing the total amounts of heat delivered between $t°$ and 20° C. For calculating these quantities also between t° and 0° C., GAEDE's measurements[1]) of c_p are made use of, which results can be represented, according to MAGNUS[2]), by the equation: $c_p = 0.031054 + 13.6 \,.\, 10^{-6} \,.\, t - 0.028 . 10^{-6} \,.\, t^2$; from this equation the value: 0.62373 is deduced for $\int_{0^\circ}^{20^\circ} c_p \,.\, dt$, so that the mean value of $\overline{c_p}$ between 0° and 20° C. is calculated to be: 0.031186. In this way the values Q_0 of the next column are calculated from the values Q. From three measurements of Q_0, for instance from those at 301°, 933° and 1546° C., we have calculated the values Q'_0 of the next column, by means of the formula:

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[1]) F. M. JAEGER and E. ROSENBOHM, These Proceedings, **30**, 905, (1927).

[2]) W. P. WHITE, Phys. Rev. (2). **12**, 436, (1918).

$$Q'_0 = 0{,}03162\, t + 0{,}00000308625\, t^2 + 0{,}000000000077751\, t^3,$$

which formula represents the values of the total amounts of heat delivered between t° and 0°, in a really excellent way.

From this formula the *true* specific heat c_p at each temperature can be then calculated by the equation:

$$c_p = \frac{dQ'_0}{dt} = 0{,}03162 + 6{,}1725 \,.\, 10^{-6}\, t + 2{,}3325 \,.\, 10^{-10} \,.\, t^2.$$

This formula cannot be used beneath 150° C.; the deviations, it is true, are even then only small, but considerably greater than the degree of accuracy here attained, which is about: 0.1 %[3]).

The obtained values of the true specific heat under constant pressure have been graphically represented in Fig. 1 up to 1620° C., as well as those from WHITE's measurements up to 1300° C. and those obtained by MAGNUS at corresponding temperatures. Notwithstanding the fact that WHITE used a different apparatus, his value, — for which he emphazises an accuracy of about 0.3 %, — appear to be *nearly completely identical* with ours: the greatest differences, which occur between 950° and 1100° C., are no more than the uncertainty of 0.3 % mentioned, while they are, for the rest, not greater than 0.15 % or 0.20 % of the total values. This complete accordance of the results can be considered as a proof of the perfect correctness of the method used here and of the results obtained. Contrary to WHITE, who represents his results by means of a straight line, we have used for that purpose a feebly bent curve, convex with respect to the temperature-axis. The values obtained by MAGNUS up to 850° C., appear to differ somewhat more; more especially his c_p-t-function, — which, as with WHITE, is assumed by him as a linear one, — appears to have a rather strongly deviating direction towards the higher temperatures,

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[1]) W. GAEDE, Phys. Zeits. **4**, 105, (1902).

[2]) A. MAGNUS, Ann. d. Physik, **48**, 998, (1915).

[3]) MAGNUS calculates the true specific heat c_p between 130° and 850° C. by means of a linear function: $c_p = 0{,}03159 + 5{,}8468 \,.\, 10^{-6} \,.\, t$. As in the temperature-interval considered here, — which has about the double extension, — the curve deviates already considerably from a straight line, we have preferred to make use of an equation with 3 constants.

TABLE I.

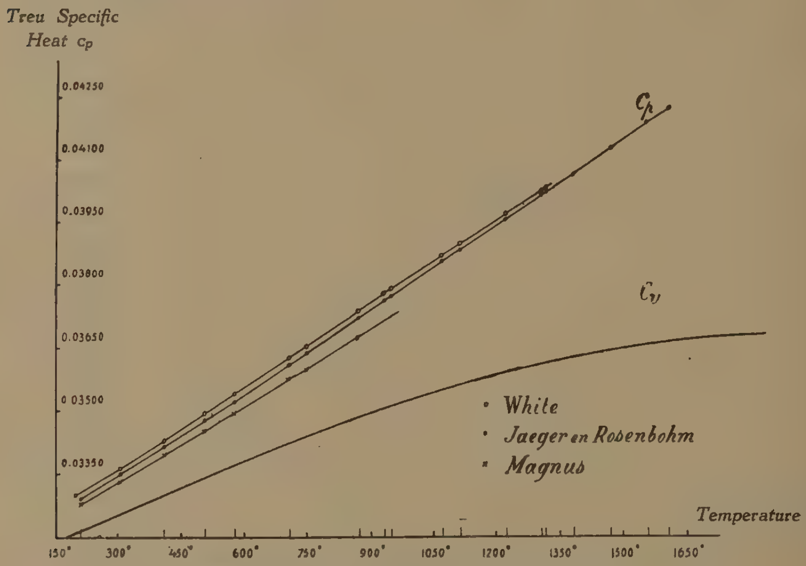
Mean and True Specific Heats under constant Pressure for Platinum between 0° (respectively: 150° C.) and 1604° C.

Temp. *t* (corr.) in ° C.:	Final temp. of calorimeter and platinum	Increase of temperature Δt observed:	Weight G of the heated platinum:	Mean specific heat $\overline{c_p}$:	Mean specific heat $\overline{c_p}$ (WHITE):	Total amount of heat delivered Q (cal.) between *t*° and 20° C. for 1 gramme of plat.:	Total amount of heat delivered Q_0 (cal.) between *t*° and 0° C. for 1 gramme of plat.:	Total amount of heat delivered Q'_0 (cal.) between *t*° and 0° C., for 1 gr. of pl. as calc. from the formula:	True specific heat c_p at *t*° C.:
100°	20°	—	—	—	0.03186	—	—	—	—
210°.7	20°.35	0°.22994	52.712	0.03247	0.03242	6.1808	6.8154	6.8000	0.03293
300°	20°	—	—	—	0.03271	—	—	—	—
301°.05	20°.59	0°.33984	52.709	0.03265	0.03271	9.1572	9.7993	9.8008	0.03350
408°.3	20°.62	0°.47467	52.706	0.03299	0.03305	12.7900	13.4330	13.4300	0.03418
500°	20°	—	—	—	0.03333	—	—	—	—
504°.8	20°.81	0°.59864	52.742	0.03330	0.03336	16.1172	16.7662	16.7583	0.03479
577°.9	20°.93	0°.69352	52.734	0.03353	0.03360	18.6750	19.3277	19.3183	0.03526
700°	20°	—	—	—	0.03399	—	—	—	—
707°.4	20°.91	0°.86486	52.714	0.03393	0.03401	23.2926	23.9447	23.9471	0.03610
747°.8	21°.14	0°.91930	52.717	0.03406	0.03414	24.7500	25.4093	25.4039	0.03637
869°.1	21°.04	1°.0844	52.742	0.03445	0.03453	29.2140	29.8701	29.8632	0.03716
900°	20°	—	—	—	0.03460	—	—	—	—
933°	21°.39	1°.1734	52.737	0.03464	0.03473	31.5786	32.2457	32.2504	0.03758
945°.7	21°.33	1°.1903	52.722	0.03468	0.03477	32.0576	32.7228	32.7286	0.03767
1068°	21°.70	1°.3625	52.725	0.03507	0.03516	36.6942	37.3709	37.3849	0.03840
1100°	20°	—	—	—	0.03523	—	—	—	—
1109°.8	21°.60	1°.4238	52.749	0.03522	0.03530	38.3200	38.9936	38.9989	0.03876
1218°	21°.80	1°.5817	52.743	0.03559	0.03565	42.5670	43.2469	43.2324	0.03948
1300°	20°	—	—	—	0.03592	—	—	—	—
1302°	21°.97	1°.7057	52.755	0.03588	0.03599	45.9260	46.6111	46.5724	0.04005
1309°	21°.91	1°.7162	52.752	0.03589	0.03594	46.1933	46.8514	46.8526	0.04010
1374°	21°.96	1°.8137	52.767	0.03610	0.03614	48.8079	49.4675	49.4741	0.04054
1464°	22°.17	1°.9509	52.795	0.03637	0.03643	52.4400	53.1314	53 1498	0.04116
1546°	22°.27	2°.0721	52.736	0.03665	0.03670	55.8445	56.5390	56.5467	0.04172
1604°	22°.41	2°.1653	52.704	0.03685	0.03688	58.2830	58.9819	58.9790	0.04212

The *true* specific heat at *t*° C. was, between 150° C. and 1604° C., calculated from the equation:

$$c_p = 0.03162 + 6.1725 \,.\, 10^{-6} \,.\, t + 2.3325 \,.\, 10^{-10} \,.\, t^2.$$

in comparison with ours. At 600° C. the divergences of his values with WHITE's and ours are already 1 %, at 850° C. about 1.5 %. Although probably these deviations are caused partially by inaccuracies in the temperature-measurements, — for MAGNUS has made use in his furnace of platinum containing *iridium*, which makes the indication of the thermocouples always more or less erroneous as a consequence of contamination, and, moreover, he has placed the hot junction of his thermo-element not *in* the crucible, but *beside* it, — it is, however, impossible that this should be the only cause. The inaccuracy in the temperature-indication would then be no less than 40° to 75°, which cannot be supposed to have been the case. It is more probable that these differences are connected in some way with accidental impurities of the metal used.



The true specific heats c_p and c_v of Platinum between 200° C. and 1650° C.

Fig. 1.

The curve for the specific heat of platinum thus obtained appears to fit very well with that representing the data at lower temperatures [1]); as a consequence the specific heat of platinum can now be considered as being exactly known from about — 255° C. up to 1625° C., i.e. within an interval of temperatures ranging over almost 1900°.

§ 2. It is a remarkable fact that up to 1600° C., there is *no* indication whatsoever of a retardation in the increase of the atomic heat under constant pressure C_p: this is found at 500° C. to be: 6.785 cal., and at 1300° C.: 7.816 cal., while at 1610° C. it is even found to be: 8.235 calories, without approaching any limit evidently. Thus, if the specific heat at constant volume c_v is calculated ¹) from the general thermodynamic equation:

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[1]) F. SIMON and W. ZEIDLER, Zeits. f. phys. Chemie, **123**, 196, (1926).

$$c_p - c_v = \frac{0{,}02345 \, . \, (3\,a)^2 \, . \, T}{\varkappa \, . \, d}$$

the considerable deviation from the theoretical value remains likewise. In this formula $(3a)$ is the cubic expansion-coefficient, T is the temperature, d the specific weight and $\varkappa$ the compressibility in kilogrammes pro cm², — all quantities to be taken at the same temperature T. The values of $3a$ are calculated from HOLBORN and DAY's formula; those of $\varkappa$ are deduced from the data of BRIDGMAN ²) and of GRÜNEISEN ³); the last mentioned investigator has emphazised a probably *linear* dependence between $\varkappa$ and t. Perhaps this extrapolation of the experimental data up to higher temperatures is not wholly allowable; but as in each case $\varkappa$ increases with the temperature, our conclusions will not be altered by eventual deviations in this respect, because the correct values of $\varkappa$ can only lie in such a direction, that the difference between c_p and c_v would appear *even smaller*, than is supposed in the following considerations. We have used BRIDGMAN's data for platinum-*wire*, which are exactly intermediate between those of GRÜNEISEN and BRIDGMAN's values for platinum in *bars*, being somewhat smaller than GRÜNEISEN's numbers; the differences are, however, only very small and the dependence of $\varkappa$ on t in all three series of experiments seems to be about the same.

In this way the following data are obtained for the specific heat at constant volume c_v and for the true atomic heat C_v of platinum between 100° C. and 1625° C. (Table II, p. 1074).

The values of c_v are also represented graphically in Fig. 1. It becomes clear in this way, that we cannot speak with certainty of any approaching of c_v to a maximum value; it is, moreover, clear that the value: $c_v = 0.03049$, corresponding to an atomic heat of $3\,R = 5.963$ calories, is

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¹) M. PLANCK, *Thermodynamik*, 2nd Edit., Leipzig, (1905), p. 118. The equation follows immediately from the general thermodynamical relation: $c_p - c_v = -T\left(\frac{\partial v}{\partial p}\right) \cdot \left(\frac{\partial v}{\partial T}\right)^2$ if it be remembered, that: $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right) = 3a$ and $\varkappa = -\frac{1}{v} \cdot \left(\frac{\partial v}{\partial p}\right)$. If $\varkappa$ is expressed in kilogrammes pro cm². (= 981 . 10³ dynes) and the calorie = 4,183 . 10⁷ ergs is adopted as heat-unity, the constant of the formula gets the value: = 0,02345. From the values of c_v, thus deduced, those of C_v can be found immediately by multiplication with the atomic weight.

²) P. W. BRIDGMAN, Proceed. Amer. Acad. of Arts and Sciences, 58, 183, (1923).

³) E. GRÜNEISEN, Ann. der Physik, (4), 33, 1264, 1268, (1910); for $\varkappa \, . \, 10^6$ we have used the values: at 100° C.: 0,367; at 500° C.: 0,401; at 1000° C.: 0,442; at 1600° C.: 0,492. The specific weight of platinum at 15° C. is: 21,34.

already attained below 0° C. The last fact clearly indicates that the supposition often made, of an "emission of electrons", cannot be considered as explaining 1) of the surpassing of the value: $3\,R$.

TABLE II.

Temperature in °C.:	True specific heat at constant volume c_v:	True atomic heat under constant pressure C_p:	True atomic heat at constant volume C_v:
100°	0.03142	6.293	6.130
200°	0.03202	6.414	6.250
300°	0.03256	6.537	6.355
400°	0.03306	6.662	6.454
500°	0.03353	6.785	6.545
600°	0.03386	6.912	6.610
700°	0.03421	7.037	6.678
800°	0.03448	7.165	6.731
900°	0.03476	7.293	6.785
1000°	0.03500	7.421	6.831
1100°	0.03527	7.552	6.884
1200°	0.03550	7.683	6.930
1300°	0.03570	7.816	6.969
1400°	0.03591	7.949	7.010
1500°	0.03610	8.081	7.046
1600°	0.03626	8.216	7.079
1700°	Extrapolated 0.03641	8.353	7.108
1755°	0.03651	8.427	7.124

Another supposition is, that the abnormally great values of the specific heats in such cases would possibly be connected with some "heat of transformation" of the metal studied, which would be superimposed upon the quantity of heat given out by the hot body. But this supposition cannot stand the test either. We may remind the reader that no indication of an

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1) E. Grüneisen, loc. cit.; F. Richarz, Zeits. f. anorg. Chemie, **59**, 156, (1908); A. Einstein, Ann. d. Physik, (4), **22**, 180, (1907); P. Debije, ibidem, (4), **39**, 789, (1912); M. Thiessen, Verh. d. d. phys. Ges., **10**, 950, (1908).

allotropic transformation in the case of platinum was ever found, although the metal has been studied in this respect with the greatest care by the best investigators in accordance with its prominent importance as material in all constructions necessary for precision-measurements (gas-thermometry; electric resistance-thermometry; thermo-electric measurements; etc.). But, moreover, the exchange of heat in our calorimeter, takes place so rapidly, that, in the case of a *slowly* proceeding allotropic transformation there is no possibility whatsoever of the superposition of any appreciable heat-effect upon that caused by the cooling of the hot object, within the very short interval of time considered here, — this being only a few seconds. It is of interest, in this respect, to remember that such heats of transformation in the solid state, are usually only rather small quantities, while here deviations need be accounted for, which at higher temperatures represent 19 % and more of the values calculated. Even in the highly improbable case that the supposed transformation would have taken place with such extreme velocity, that it would have been completely finished within the few seconds in which the total heat-exchange between the heated object and the calorimeter has occurred, — a case in which a distinction made between a really "unary" and a "pseudo-unary" system would no longer have any real significance, — such great amounts of heat could not possibly have been given of in excess for all that. Moreover, in this case and in that of *tungsten*, where the same phenomenon is repeated, we have heated samples of the pure metals during a long time at constant temperatures and than quenched suddenly in cold oil or mercury; the samples thus treated were then studied by means of *X*-rays. But in the spectrograms thus obtained before or after the heating and quenching, *no* alterations whatsoever, be it in the intensity or in the place of the diffraction-lines, could be observed. Thus, for instance, the spectrogram (after HULL-DEBIJE; *Cu*-*α*-radiation) of a sample of the purest, pulverized platinum, which was heated at 1200° C. during several hours and then quenched in oil of 15° C., appeared to have the same diffraction-images with the same relative intensities, and the same grating-constant a_0, as a sample which had not been heated beforehand.

And this complete identity of the spectrograms was also stated in the case of tungsten, heated at 700° C. during several hours, in comparison with that of a sample at room-temperature: no indication whatsoever could be found of any change in structure or in density of the metal considered here. Therefore, the hypothesis mentioned before, must, in our opinion, totally be rejected.

Such discrepancies between the experimental data and the theoretical views as stated here, have in a few cases been found already by earlier investigators; but bij the present, very accurate measurements up to 1600° C., these facts are now put beyond any doubt and cannot be ascribed any longer to experimental errors. Neither appears there to exist, as GRÜNEISEN (loco cit.) first pointed out, a constant ratio between the linear expansion-coefficient α and c_p as, in the case of platinum, may be seen from the following data :

Temperature in °C.:	Ratio $\frac{\alpha}{c_p} . 10^6$:
0°	285.6
300°	276.7
800°	270.4
1300°	264.7
1600°	261.0

Evidently the ratio mentioned diminishes gradually with increasing temperatures, and this diminuition appears to be no linear function of the temperature.

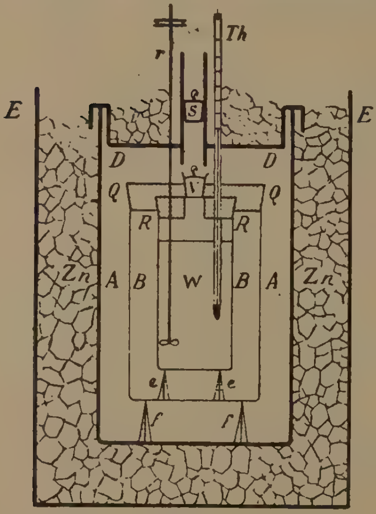

Fig. 2.

§ 3. As in these measurements and the others it appeared to be necessary to reduce the measurements between $t°$ and 20° C., to such between $t°$ and 0° C., — it was necessary, therefore, to extend the method of measurement of c_p also between 20° and 0° C. For this purpose a separate calorimeter of simple construction was made use of, which instrument is schematically reproduced in fig. 2.

In a cylindrical vessel *E*, made of enamelled iron, and filled with small lumps of ice, a vessel *Zn* is placed coaxially. This vessel is made of plated zinc and shut by a lid *D*, equally filled with ice. A tube of porcelain, which can be closed by a stopper *S*, passes this cover as well as a stirrer *r* and a calibrated BECKMANN-thermometer Th, which has scale-divisions of 0°.001 C.

Within the vessel *Zn* and separated from it by two supports *f* and *e*, made from ebonite, a double-walled vessel *A B* of plated copper is placed coaxially with *E* and *Zn* ; the wall *A* is *internally*, the wall *B* *externally* polished as perfectly smooth as possible. *B* contains 200 grammes of water *W*, into which the stirrer *r* and the BECKMANN-thermometer are immerged ; the heat of the object introduced is given out to this water. *A* and *B* are both closed by means of ebonite covers *Q* and *R*, which have a coaxial central perforation, the cylindrical channel of which can be shut by means of a stopper V.

The object to be investigated is heated within a test-tube, which is placed within a waterbath with double walls and of such a construction, that it can be completely reversed at the moment, that the object heated at an accurately fixed temperature between 0° and 100° C., is dropped without any loss of heat into the porcelain tube of the calorimeter ; and so, by instantaneous opening of the stoppers S and V, is introduced into the water of B. The required determinations take place in the wellknown way, as followed in the case of the usual calorimeters containing a liquid : the degree of accuracy reached is, although not so great as in the case of the big metal-calorimeter, plainly sufficient for determining the only small correction necessary for reducing the measurements to 0° C., in stead of to 20° C.

§ 4. In the second place the specific heat of pure *tungsten* was determined by us in the same way. We had at our disposal the crystallized metal in a perfectly pure condition in the form of a thick prismatic bar ; for it, and for some other metals we are obliged to Dr. HOLST and Dr. DE BOER of the laboratory of PHILIPS' *Incandescent Lamp-Manufacture* at *Eindhoven*, to whom we once more wish to offer our sincere thanks also here again.

The measurement of the specific heat of *tungsten* at higher temperatures appeared to involve many difficulties, which are chiefly caused by the fact, that the metal at temperatures exceeding 600° C., is very easily oxydized. The oxydation-product formed, which at lower temperatures is chiefly WO_3, is above 900° C. by loss of oxygen gradually transformed into a dark, indigo-blue mixture of oxides, which, in its turn, at still higher temperatures is transformed into a pale greenish, beautifully crystallized mixture of other oxides, the composition of which are undetermined and which , moreover, at temperatures surpassing 1300° C., appear to be so volatile and consequently to sublime so rapidly, that up till now, all measurements had to be stopped at 1300° C. The sublimate thus generated, vehemently and very rapidly attacks the protective tubes of hard porcelain of the thermocouples and the parts of the furnaces containing silica and alumina ; it was, therefore, also impossible to make use of a porcelain lining in the platinum crucible, in which the metal was heated here. Up to 1300° C., — this being the highest temperature in this case, to which the measurements of c_p with *tungsten* could be extended, — platinum happily appeared *not* to be attached, however, by the heated metal, nor by one of its oxides ; therefore, the said protective lining could, finally, be completely omitted here. The *tungsten* was brought into the shape of a compact, conical mass, weighing more than 52 grammes and exactly fitting into the platinum crucible ; this lump was then cut into two halves parallel to a median plane, which, in the direction of the axis, were both provided with a half-cylindrical excavation, thus forming together a channel through which passed the prolongation of the platinum hook, by the aid of which the crucible was suspended in the furnace. Moreover, along the inner wall of the crucible, in *one* of the halves of the *tungsten*-piece also a cylindrical furrow was cut, in which fitted a small, thin platinum tube, fixed to the cover of the crucible and destined to hold the junction of the thermo-couple. In each measurement successively the following data were accurately determined : *a*. the weight of the platinum crucible with its cover before and after each experiment ; *b*. the weight of the *tungsten* before the experiment ; *c*. the increase of weight of the *tungsten* after the experiment, as a consequence of its oxydation ; *d*. the final weight of the remaining *tungsten* and that of the oxides formed in the experiment, being both first separated from each other as completely as possible.

The specific heat of WO_3 at lower temperatures was also measured. Soon it became clear, however, that by loss of oxygen, besides this oxide, a number of lower oxides of unknown composition is formed (W_2O_5, WO_2 ?), forming together the components of a mixture at each temperature in equilibrium and recognizable by particular colours, ranging from pale yellow to dark indigo-blue, intermedially, passing through yellowish grey and a dull green hues ; above 1300° C. this mixture is finally transformed into a beautifully crystallized, pale greenish and highly volatile mass. As the composition of the intermixed oxides and their mixing ratio are unknown, the correction of the observed data, necessary as a consequence of the oxidation of the metal, could only be applied by measuring preliminarily the specific heat of the mixtures of oxides, obtained by heating the tungsten-oxide during a long time *at exactly the same temperatures* as those at which the specific heat of the metal was determined, so that equilibrium was really established. As in the measurements executed with the metal, every time the total quantity of the mixture of oxides formed was determined, it was possible to apply the small correction looked for, as soon as the specific heats of the equilibrium-mixtures of the oxides were known.

In the following Table III the results are put together, obtained in the measurement of the specific heats of WO_3 and of the *yellowish green* mixtures of oxides between 500° and 900° C. ; those, of the specific heat measurement between 1000° and 1300° C. ; of the *blue* mixtures of oxides, produced above 925° C., and, finally, the data concerning the specific heat of the *yellowish green* mixtures of oxides between 20° C. and 2°.70 C., which last numbers were obtained by means of the apparatus reproduced in Fig. 2. Although not complete, these data are fully satisfactory for the said purpose. Calculations show, that between 0° and 900° C. the true specific heat c_p of the *yellowish green* mixtures of oxides at each temperature $t°$ can be readily expressed by the formula :

$$c_p = 0.0503755 + 0.13644 \,.\, 10^{-3} \,.\, t - 0.0490476 \,.\, 10^{-6} \,.\, t^2.$$

If this formula be applied for the calculation of the *mean* specific heats

TABLE III.

Determination of the mean specific heat of the yellowish green and of the blue mixtures of tungsten-oxides between 0° and 1300° C.

A. Yellowish-green mixtures of oxydes.

1. Mean specific heat between 2°.70 C. and 20°.38 C.: $\bar{c}_p = 0.0558$. 1)
2. Measurements above 500° C.:

Weight (in grammes) of platinum crucible (g) and of the mixture of oxides (p):	Final temperature of the calorimeter:	Furnace-temperature:	Δt	$\bar{c}_{Pt} \cdot m_{Pt} + \bar{c}_{Ox} \cdot m_{Ox}$:	Mean spec. heat $\bar{c}_p$ of the mixture of oxides:
$g = 23.2696$; $p = 8.1810$	20°.48	516°	0°.5063	0.7756 + 0.6757	0.08259
$g = 23.2696$; $p = 8.1816$	20°.73	721°	0°.7625	0.7907 + 0.7556	0.09235
$g = 23.2720$; $p = 8.1861$	20°.99	908°	1°.0141	0.8043 + 0.8192	0.10007
B. Dark blue mixtures of oxides.					
$g = 23.1000$; $p = 15.3448$ 2)	21°.78	1097°	1°.8024	0.8124 + 1.5673	0.1021
$g = 23.1070$; $p = 15.3634$	22°.16	1292°	2°.1842	0.8284 + 1.6140	0.1050

of the *blue* mixture of oxides at 1097° C. or 1292° C. respectively, then the values calculated 3) in this way appear to be considerably greater than those observed. This means, that indeed, above 925° C. other solid phases have appeared in the dark blue mixture, for which there exists another connection between the specific heat and the temperature, than that, which is valid in the case of the yellowish-green oxides.

§ 5. With the aid of all these data, it was now possible to determine the specific heat of metallic *tungsten* up till 1300° C. as completely as possible. The respective data are collected in Table IV.

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1) In this experiment we used 12.7052 grammes of the yellowish-green mixture of oxides in a brass vessel weighing 4.6392 grammes.

2) The crucible contains about twice the weight of oxides mentioned sub A, as a consequence of the much greater density of the blue oxides in comparison with that of the yellowish-green ones.

3) If the total amount be taken into account, which is given out by the yellowish green mixture of oxides between 20° and 0° C., — then for Q_0, i.e. the total amount of heat given out by 1 gramme of the mixture of oxides between $t°$ and 0° C., — the values are found: at 516° C., $Q_0 = 41.9115$ calories; at 721° C., $Q_0 = 65.6567$ calories; and at 908° C., $Q_0 = 89.7466$ calories.

By experiment for the blue mixture of oxides a value of Q_0 is found of about 111 calories by 1097° C., and of 134.5 calories at 1292° C. But if the equation mentioned, in its integrated form, remained valid also for the blue mixtures, then the data 116, resp. 144 calories are calculated, — which values are 4 to 7 % too high.

TABLE IV. The mean and true specific heat under constant pressure of tungsten between 0° C. and 1300° C.

A. Measurements of the specific heat of *tungsten* between 0° C. and 85° C.

Used 1.3054 grammes of the metal. For the *mean* specific heat $\overline{c_p}$ were found the following numbers:

between 19°.45 C. and 0°.42 C.: $\overline{c_p} = 0.0271$.
between 53°.75 C. and 0°.79 C.: $\overline{c_p} = 0.0276$.
between 83°.79 C. and 0°.46 C.: $\overline{c_p} = 0.0278$.

The *true* specific heat between 0° and 85° C. can be represented by: $c_p = 0.02659 + 0.0000694 \, . \, t$.

B. Measurements between 300° and 1300° C.

Corr. Furnace-temperature in °C.:	Final temperature of the calorimeter:	Δt (increase of temp. observed):	G = Weight of platinum g = Weight of tungsten p = Weight of mixture of oxides	$\overline{c_{Pt}} \, . \, m_{Pt} + \overline{c_w} \, . \, m_w + \overline{c_{ox}} \, . \, m_{ox}$:	Mean specific heat of tungsten $\overline{c_p}$:	Q (cal.) Total amount of heat delivered by 1 gr. tungsten between t° and 20° C.:	Q_0 (cal.) Total amount of heat delivered by 1 gr. tungsten between t° and 0° C.:	Q'_0 (cal.) Values of Q_0 from formula:	True specific heat c_p of tungsten at t° C.:
306°.7	20°.48	0°.4656	G = 23.292 Gr. g = 52.249 Gr.	0.7609+1.5492=2.3101	0.02958	8.4664	9.0327	9.0324	t°: c_p: 100° 0.0287^6
408°	20°.59	0°.6408	G = 23.292 Gr. g = 52.249 Gr.	0.7684+1.5804=2.3488	0.03025	11.7192	12.2885	12.2837	200° 0.0300^6 300° 0.0313^6
505°	20°.71	$0°.8144^4$	G = 23.292 Gr. g = 52.249 Gr.	0.7756+1.6125=2.3881	0.03086	14.9452	15.5179	15.5099	400° 0.0326^4 500° 0.0339^3
602°	20°.95	$0°.9926^2$	G = 23.270 Gr. g = 52.251 Gr.	0.7819+1.6439=2.4258	0.03146	18.2800	18.8593	18.8796	600° 0.0352^2 700° 0.0365^1
721°	21°.16	1°.2222	G = 23.265 Gr. g = 51.516 Gr. p = 0.342 Gr.	0.7906+1.6576+0.0316 = = 2.4798	0.03218	22.5211	23.1062	23.1650	800° 0.0378^2 900° 0.0391^4
909°	21°.54	1°.5866	G = 23.268 Gr. g = 49.898 Gr. p = 0.659 Gr.	0.8044+1.6685+0.0659= = 2.5388	0.03347	29.7036	30.2992	30.3113	1000° 0.0404^7 1100° 0.0418^3
1097°	22°.06	2°.1094	G = 23.281 Gr. g = 51.399 Gr. p = 1.827 Gr.	0.8188+1.7808+0.1866= = 2.7862	0.03469	37.2891	37.8991	37.9286	1200° 0.0432^2 1300° $0\ 0446^3$
1292°	22°.80	2°.4132	G = 23.312 Gr. g = 47.196 Gr.	0.8357+1.6918+0.1714= = 2.6989	0.03587	45.5259	46.1563	46.3411	

The values of Q'_0 can with sufficient accuracy be represented by the equation:

$$Q'_0 = 0.0274412 \,.\, t + 0.066336 \,.\, 10^{-4} \,.\, t^2 - 0.030496 \,.\, 10^{-8} \,.\, t^3 + \\ + 0.016953 \,.\, 10^{-11} \,.\, t^4.$$

The *true specific heat c_p of tungsten* at each temperature of $t°$ C., can, therefore, be calculated from:

$$c_p = 0.0274412 + 0.132672 \,.\, 10^{-4}\, t - 0.091488 \,.\, 10^{-8} \,.\, t^2 + \\ + 0.067812 \,.\, 10^{-11} \,.\, t^3.$$

The values of c_p calculated in this way are reproduced in Table IV in the last column; the coefficients of t^2 and t^3 have a small influence only, but cause the temperature-coefficient of c_p to increase gradually at higher temperatures, although only very slowly.

In Fig. 3 these values are reproduced graphically in their dependence on t: the curve appears readily to be substituted for practical purposes by a straight line, thus c_p being sufficiently accurately expressed by the linear function:

$$c_p = 0.02744 + 0.0000132 \,.\, t.$$

The curve is only slightly concave towards the upper side of the figure.

§ 6. The values of c_p determined here strongly deviate from those obtained formerly by other investigators by means of *indirect* methods, and especially by measurements executed with evacuated electric incandescent lamps [1]). In a method originally proposed by CORBINO, later-on improved by WORTHING and GAEHR, and applied with some variations by SMITH and BIGLER, and by BOCKSTHALER, use is made of observations of the changes in radiation, in electrical resistance and in temperature of a thin tungsten-wire, in their dependence on the time elapsed since the moment, at which the current-intensity in the wire is suddenly altered. Although the method is ingenious in its device, it cannot give the conviction of its allowing the exact and reproducible determination of the values of c_p. In the equations valid here, c_p enters only as a factor in a single term standing besides some others, in which a considerable percentage of the whole effect observed is expressed. Moreover, the method is very complicated and there are many sources of error; so that the lack of agreement of the data of different observers and even of the same observer at different temperatures, as well as the mysterious discrepancies in the cases that the wire is either heated or cooled, in connection with the necessity of measuring the temperature of the wire at any moment by means of an optical pyrometer, etc., — are so many circumstances to rouse serious doubts about the reliability of the whole method and the results obtained by it. On the contrary, in our *direct* and thoroughly perfect determinations of the specific heat, experimental errors of any considerable size are excluded beforehand; so that they can only be considered as of secondary significance in the explanation of the differences mentioned above. Moreover, up till 721° C., the oxydation of the compact, crystallized metal does not yet play a role of any importance, the correction for it being, therefore, negligible even at this temperature; the results obtained between 0° and 20° C. by direct measurement are in full agreement with the best data found in literature and those above 721° C. are as perfectly fitting in with the values for c_p determined below 721° C., as can be desired. We have the conviction, therefore, that the data gathered here by us by the aid of *direct* measurements, are to be considered as much more reliable than those obtained by the *indirect* methods described in the above.

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[1]) M. v. PIRANI, Verh. d. d. phys. Ges. **14**. 375, (1912); O. M. CORBINO, Phys. Zeits., **13**, 375 (1912); A. G. WORTHING, Phys. Review, (2), **12**, 199 (1918); P. F. GAEHR, ibidem, 396; K. K. SMITH and P. W. BIGLER, ibid., **19**, (1922), 268; L. J. BOCKSTHALER, ibid., **25**, (1925), 677.

§ 7. On the other hand, MAGNUS and DANZ [1]) have recently published the results of a number of measurements, — also *direct*, — of the specific heat of *tungsten* between 400° and 900° C., which, however, are in complete disagreement with ours. They find, it is true, also a *linear* dependence between c_p and t; but the straight line by which their results are represented graphically, is much less steep than ours, although their values are considerably greater, so that the said straight line of the German investigators in its whole extension is situated far *above* that of Fig. 3. At 600° C. their value for c_p is about 13 %, at 100° C. no less than 30 % greater than ours; moreover, they calculate, *by extrapolation*, a value for c_p at 0° C. of: 0.03685, which is about 34 % too high in comparison with our value really *measured* at that temperature, — which value, as has been remarked, is in close agreement with that of other observers. In connection with these data, they find then, furthermore, the abnormally high values of the atomic heat C_p published by them: at 0° C. this value would already be: 6.78, and attain even: 7.7 at 900° C.; etc.

In our opinion, the cause of this apparent incompatibility of results and of the abnormal values for C_p is easily understood, if the difficulties met with in these measurements, as described in the above, be remembered. In the first place an inaccuracy in the indication of the temperatures, as a consequence of the use of iridium-containing platinum in the furnace, may again have had some influence. But of much more importance is the fact, that MAGNUS and DANZ have repeatedly made use in their experiments of heated tungsten in *powder*-form. In the beginning of our experiments already it became quite clear to us, that the metal in powder-form is absolutely inappropriate to this kind of measurements: not only, that on heating equal weights of tungsten in powder-form and as a compact, crystallized metallic bar at 1000° C. during 15 minutes, was in the first mentioned case *totally* converted into an oxydation-product, while in the second case it was *only at its outer surface* coated with a thin layer of oxides; but, moreover, we found that the metal in powder-form on being heated for a long time at so low a temperature as 300° C. only, was for by far the greater part already oxydized, while the compact bar, being of the nature of one single crystal, was not yet attacked at all. Therefore, in using the metal in powder-form, MAGNUS and DANZ already after their first heating it at 600° C., must have experimented with a preparation, which for by far its greater part must have consisted of a mixture of oxides; and in their successive experiments, this must have been converted almost completely into those mixtures of oxides, which at the same temperatures exist in equilibrium with the metal. In their measurements, therefore, probably no metallic tungsten at all was present any more; thus, not only the ratio *Wo* : *Wo-oxide* was altered, as they suppose, during their experiments, but also the *degree* of oxidation of the mixture was changed. And that there is here not only a question of *one* single oxide WO_3, but of a complete mixture of *several* oxides, the composition of which depends on the particular circumstances during the heating, — has been fully demonstrated by us by a series of experiments. Already at 600° C. the results obtained appeared to be quite erroneous, if the quantity of oxide formed was calculated from the amount of oxygen taken up by the sample, under the wrong assumption, that exclusively WO_3 was formed in this case. It is exactly because of these experiences in the true nature of these oxidation-processes, that we finally passed on to determine the specific heats of the equilibrium-*mixtures* of these oxides separately and to measure not only the amount of oxygen taken up, but also the weight of the remaining metal and that of the mixture formed, for the purpose of applying the necessary corrections. The too high results of the German observers are fully comprehensible from the mere fact, that the specific heats of these mixtures of oxides are, at each temperature, *much higher* than those of the tungsten itself. It becomes also clear in this way, why their c_p—t-line, obtained by an *extrapolation* towards lower temperatures from wrong values observed at higher ones, must be entirely be situated *above* the normal straight line: for the observed values used do not bear upon the metal itself, but on the *much higher* values for the mixture of oxides, — or for this plus some remaining metal, — which at the same temperatures coexist. It is clear that this extrapolation must then lead to values at lower temperatures, which are much too high, so that the straight line drawn in this way must have a much less steeper inclination with respect to the t-axis, than that obtained by us by direct measurements. Neither does the value of c_p at 0° C. published by the said authors agree with the value found by direct measurement at that temperature.

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[1]) A. MAGNUS and H. DANZ, Ann. der Physik, **20**, 415, (1926).

§ 8. If now we consider the dependence stated here of the specific heat of tungsten on the temperature, we can say that there appears to be present no indication whatsoever of an eventually occurring allotropic transformation of the metal between 100° and 1300° C. From the behaviour of tungsten towards elastic and stretching forces, some American investigators [1]) of the *General Electrical Company in Schenectady* were induced, however, to assume the presence of a kind of transformation-points at about 560° C. and at 1375° C., at which temperatures the metal seemed to manifest certain discontinuities in its tensile strength, etc. considered as a function of the temperature. But in connection with those experiments, it remains highly doubtful, whether the mechanical properties of the metal under these circumstances must be ascribed to a mere change in the mutual orientation of the microscopical crystalline individuals with respects to each other under the influence of the applied external forces, or whether real "allotropic transformations", — in the sense of the doctrine of heterogeneous equilibria, — are taking place here. The American authors try to corroborate their view by means of a particular interpretation of their results of the measurements regarding the thermal expansion of the metal. These numerical results are, it must be remarked, in perfect agreement with those formerly obtained by WORTHING [2]) and expressed by him between 300° (abs.) and $T°$ (abs.) by means of the formula:

$$L_T = L_{300} \{1 + 4.44 \,.\, 10^{-6} \,.\, (T-300) + \\ + 4.50 \,.\, 10^{-11} \,.\, (T-300)^2 + 2.2 \,.\, 10^{-13} (T-300)^3\},$$

in which L_T is the length of the tungsten-bar at T^0 (abs.) and L_{300} at 300° C. abs.

The dependence of the linear thermal expansion-coefficient a on t (in ° C.), can, therefore, also be represented by the expression:

$$a \,.\, 10^6 = 4.4402 + 0.09034 \,.\, 10^{-3} \,.\, t + 0.663 \,.\, 10^{-6} \,.\, t^2$$

Now the American investigators divide this curve into *three* separate parts, along which a and t would show a linear dependence: between 100° and 577° C. this coefficient would constantly be: $a = 4.50 \,.\, 10^{-6}$; between 577° and 1377° C., $a \,.\, 10^6$ would be: 5.20 till 5.70; while above 1377° (up to 2220° C.) a would be: $7.27 \,.\, 10^{-6}$. Now it is clear, that it remains wholly questionable, whether such a division of a curve into rectilinear parts in this way, has any real sense at all, and whether this has not occurred solely with the purpose to give an apparently stronger support to the premise, that the results of the measurements of the tensile strength as a function of the temperature must run parallel with an analogous localisation of discontinuities in the temperature-functions of other properties also of the metal studied. The *exposition* given is not suitable indeed, to convince the reader of the exactness of the view proposed.

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[1]) Phil. Mag. **48**, 245 (1924); cf. p. 245 and 246.

[2]) A. G. WORTHING, Phys. Rev., (2) **10**, 638 (1917).

In every case it is quite certain, that in our results concerning the specific heat of tungsten and its practically linear dependence on temperature, there can be no question of any discontinuity manifesting itself at 550° or 570° C.; above 1300° C. the experiments were not continued because of the reasons already mentioned, so that a decision about the occurrence or non-occurrence of a transition-temperature above 1375° C., could as yet not be taken with certainty. Moreover, the ROENTGENographic study of the heated tungsten, as formerly described, gives full proof of the fact, that *no* allotropic transformation occurs between 560° and 700° C.

§ 9. By means of the same general relation as that mentioned in the case of platinum, we have calculated the values of c_v at each temperature from those of c_p. For the calculation of the cubic expansion-coefficient of tungsten, we have made use of WORTHING's formula for the linear expansion, because this gives numbers identical with the measurements of the observers of the *General Electrical Company* mentioned above. Moreover, measurements of the compressibility $\varkappa$ are made by BRIDGMAN [1]), though only for two temperatures: 30° and 75° C. But in the first instance, it is, according to GRÜNEISEN's arguments, highly improbable, that appreciable deviations of linearity would be present here; moreover, the temperature-coefficient of $\varkappa$ is only very small, and as a consequence of the small thermal expansion, the whole correction-term for $(c_p—c_v)$ has, in the case of tungsten, a small value only. Therefore, the principally unallowable extrapolation of the supposed linear $\varkappa$—t-function can only cause insignificant errors, and the real values of c_v can, moreover, be only somewhat greater, but cannot be smaller than those calculated here in this way: for the correct values of $\varkappa$ can be only greater than those used here, so that, in that case, $(c_p—c_v)$ would be still smaller, than it has been found to be here.

If these considerations are taken into account, and if for the specific weight of tungsten in bars at 15° C. the value: 19.137 is adopted, the values of c_v and the corresponding ones of the *atomic heat*: $A . c_v$, are calculated from our measurements of c_p for a series of temperatures between 100° and 1300° C. and put together in *Table V*. Moreover, the values of c_p and c_v in their dependence on the temperature, are graphically represented in Fig. 3, from which the practically *linear* course of both curves is immediately seen.

From these data it becomes clear, in the first place that, — just as in the case of platinum, — the maximum value of $3R = 5.963$ calories is already attained at a relatively low temperature (about 400° C. here) and gradually increases to 7.99 or 8.0 calories at 1300° C. As c_v varies practically with t in a *linear* way, no indication is found of a gradually

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[1]) P. W. BRIDGMAN, Proceed. Amer. Acad. of Arts and Sciences, **58**, 165 (1923); idem, Proceed. of the Nat. Acad. of Sciences, **8**, 362 (1922); **10**, 412 (1924).

TABLE V.

Values of the true specific heat of tungsten at constant volume and of the atomic heat: $A \cdot c_v$ at temperatures between 0° and 1300° C.:

Temperature in °C.:	c_v (in calor.):	Atomic heat C_v (in calor.):
0°	0.02730	5.023
100°	0.02847	5.239
200°	0.02976	5.476
300°	0.03098	5.700
400°	0.03229	5.941
500°	0.03355	6.173
600°	0.03475	6.394
700°	0.03601	6.625
800°	0.03724	6.853
900°	0.03850	7.084
1000°	0.03958	7.283
1100°	0.04066	7.482
1200°	0.04162	7.658
1300°	0.04347	7.998

approaching a limiting value at higher temperatures, and in appearance there is probably no such limiting value at all. From these results in the case of platinum, as well of tungsten, the conclusion must again be drawn, that the modern theories of specific heat postulating the existence of such a limiting value of $3R$ for the atomic heat at constant volume, cannot be right. BORN and BRODY [1]) have tried to give such an extension to the considerations of the theory of quanta leading to those theories of specific heat, as to make this limiting condition unnecessary.

Taking into account the unharmonic character of the oscillations at higher temperatures, at which the amplitudes of the oscillators become rather great, they are able to derive an equation for C_v of the form: $C_v = 3R(1-6 . \sigma . RT)$, in which σ can ordinarily be *negative*, according to these authors, so that C_v might eventually surpass the value of $3R$. The factor $\sigma = \sigma' + \sigma''$, of which terms σ' is always < 0 and $\sigma'' > 0$, the sum of both being negative, therefore, if the absolute value of σ' be greater than that of σ''. But σ' is connected with the terms for the potential energy of the system of the 3rd, σ'' with those of the 4th order, the factors represented by σ' allowing more in particular for the *thermal expansion* of the substance. From this the conclusion must be drawn, that such a linear increase of C_v

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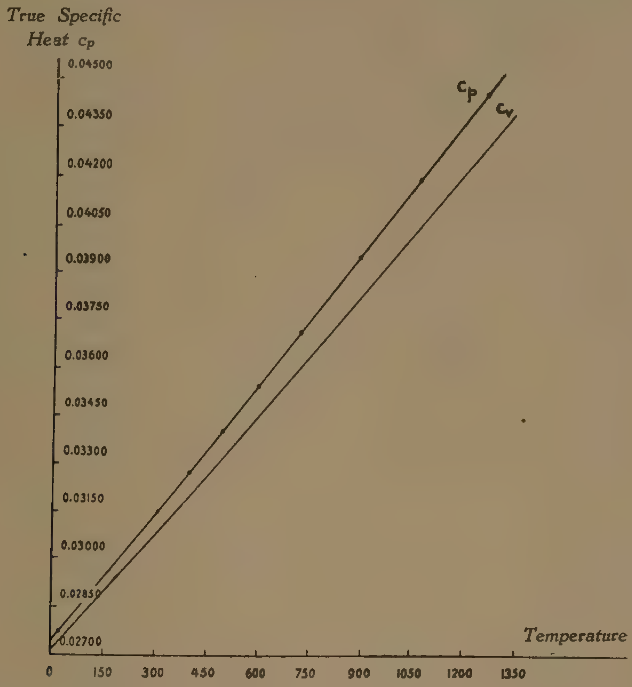
[1]) M. BORN and E. BRODY, Zeits. f. Physik, 6 (1921), 136.



The true specific heats c_p and c_v of Tungsten between 0° C. and 1300° C.

Fig. 3.

and t above the value $3R$, would occur principally with substances, whose thermal expansion is considerable.

Our experiments teach us the opposite : exactly in the case of *platinum* with its very *small* expansion-coefficient and even more so in the case of *tungsten*, whose thermal expansion-coefficient is still smaller, we found the greater deviations. The extension of the theory mentioned, therefore, cannot yet satisfactorily account for the true behaviour of these substances at higher temperatures, which phenomena are now established here beyond all doubt [1]).

Therefore, if these phenomena should appear to be generally observed, it would be inevitable to modify the fundamental conceptions

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[1]) In a recent paper (*Die Naturwissenschaften*, **15**, (1927) 825), A. SOMMERFELD points out, that the electronic motion of the metal at higher temperatures, can probably contribute no more than about $1/100 \, . \, R$ to the increase of C_v above the supposed maximum value.

conceptions of the theory in such a way, that the limiting condition in it, discussed in the above, can be eliminated from it, although in that case no rational explanation of DULONG and PETIT's well-known empirical rule could any longer be given.

We are occupied in extending these investigations also to other chemical elements.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Physics. — *On the Variability of Old Standard Kilogrammes.* By Prof. L. H. SIERTSEMA. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of October 29, 1927)

In 1886 a number of old standard kilogrammes were weighed by J. A. C. OUDEMANS [1]), who examined at the same time in how far these had changed in value after a great number of years. The preparation of standard kilogrammes for the Inspection of Weights and Measures by the Committee of Supervision of the standards of the metre and the kilogramme (kilogramme-metre Committee), through which the Committee at the same time came into possession of secondary standards, which had been compared with the Dutch platinum-standard kilogramme, was an inducement to undertake again a similar investigation. The variability of the kilogrammes weighed by OUDEMANS could now be ascertained more fully than before, since more earlier weighings, and more reliable ones are at our disposal in consequence of OUDEMANS' work.

Besides OUDEMANS' weights a number of others have been included in the investigation.

The determinations of weight have been performed with a simple balance of BECKER's Sons of the physical laboratory of the Technical University at Delft. This balance has no particularly great sensitiveness, but on the other hand it is very constant. The graduation, in mm, was read with a telescope, erected at about a metre's distance from the balance, to $^1/_{20}$ of the scalar divisions. Each position of equilibrium was derived from three points of inversion taken as soon as the series of points of inversion showed regularity. The weighing has further been performed according to GAUSS' method of transposition. After a position of equilibrium had been determined a few times with sufficient uniformity, the weights were changed, again positions of equilibrium were determined, and this was continued till a series of values was obtained, which were in good harmony with each other. Then a scalar value was determined. Before and after each series of weighings two thermometers and a hygrometer, which were placed in the balance case, and a mercury barometer, erected in the same room, were read.

Of a couple of the weights examined the volume was not known, so this had to be determined first. For this purpose the same balance was used with auxiliary apparatus for hydrostatic weighing corresponding to those that have been used for similar weighing experiments in the Bureau international des Poids et Mesures [2]). In such weighing there is almost always some loss of weight, which amounted to as high a value as 12 mg in weighings of kilogramme-weights by Stamkart 1). In order to eliminate a possible cause of this, care was always taken that the weights in the water rested on amber, so that there is no conductive connection with the metal of the suspending frame, and no danger of electrolytic actions. Before the hydrostatic weighing the weights have been carefully weighed, so that their loss of weight is known. It has appeared that, as Oudemans found, there was in the older weights always an appreciable loss, probably because in the course of years the surface of the weights will not have remained perfectly clean, and was cleaned now. In new weights the variation of weight was, on the contrary, insignificant.

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[1]) Versl. en Med. K. Akad. v. Wet. Amsterdam, (3) 3 (1887) p. 141; 4 (1888) p. 97.

[2]) Cf. Trav. et Mém. du Bureau int. des poids et mesures part 2.

In the table on the next page all the weights treated, also the above-mentioned standards of the Committee and the standards of the State Mint, have been inserted.

Most of these weights have been treated in papers by Moll 2), Stamkart 3), Oudemans, and Hoitsema 4), and kindly put at my disposal by the said institutions for this investigation. It is noteworthy that the kilogrammes L_{10}, v Sw and Aen, made by Fortin, were brought from Paris by Van Swinden in 1799, thus being among the oldest kilogramme-weights. The weight L_{10} was then presented to the government of the Batavian Republic, and served as legal standard of weight from 1819 to 1839.

The weights A, B, and C came from Paris with the platinum standard kilogramme in 1839.

The weights have been combined into groups of four or five, of which every weight was compared with each of the others, and from which then the difference of weight with one of them was derived. Thus the following groups were formed. The mean error reached is every time indicated. By Pt the Dutch platinum standard kilogramme is denoted: for its volume 47122 mm^3 is taken at 15° C.

Groups :	I, II, III, P″, Pt	m.e. = 0.06 mg
	A, B, C, P″	„ = 0.06 „
	L_1, L_2, L_3, I	„ = 0.11 „
	L_{10}, v Sw, Aen, II	„ = 0.07 „
	F_1, F_2, G_2, I	„ = 0.09 „
	St 1, St 2, St 5, I	„ = 0.08 „
	Sl, Contr, Del, I	„ = 0.07 „
	St 6, St 7, K I, I	„ = 0.05 „

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1) Cf. Oudemans, Versl. en Med. K. Akad. v. Wet. Amsterdam, (3) 3 (1887) p. 173.

2) G. Moll, Bijdragen tot de natuurk. wetensch. **6** (1831) p. 119.

3) F. J. Stamkart, Cf. Versl. en Med. K. Akad. v. Wet. Amsterdam, **6** (1857) p. 92; **7** (1858) p. 32.

4) C. Hoitsema, Muntverslag over 1902, p. 113.

A. BRASS WEIGHTS.

	Old name	Property of	Prepared in	Form	Surface	Remarks
I		Committee	1909	sphere	gilt	Secondary standard
II		„	„	„	„	„ „ 1)
III		„	„	„	„	„ „
L$_{10}$		Insp. W. and Meas.	1799	cyl. w. knob	bare	Legal stand. 1819—1839
v Sw	kg of v. Swinden	Nat. lab. Utrecht	„	„	„	
Aen	kg of Aeneae	Insp. W. and Meas.	„	„	„	
F$_1$	kg of Fortin	Nat. lab. Utrecht	± 1800	„	„	
F$_2$	kg of Fortin	Insp. W. and Meas.	± 1800	„	„	
M	kg of Gandolfi	State Mint	± 1810	„	„	
Sl	Slaper	„ „	1818	„	lacquered	
Contr	Contraslaper	„ „	„	„	„	
A		Insp. W. and Meas.	1838	cylinder	bare	
B		Nat. lab. Leiden	„	„	„	
C		Insp. W. and Meas.	„	„	„	
Del	kg of Deleuil	State Mint	1837	cyl. w. knob	„	
S		„ „	1839	„	lacquered	
L$_1$		Nat. lab. Leiden	1838	„	„	
L$_2$		„ „ „	unknown	„	„	
L$_3$		„ „ „	„	„	„	
K I		K. Ak. v. Wet.	„	„	bare	
St 1	Nº 1 (Oudemans)	Teyler's Gen.	1856	cylinder with screwed-on kn	gilt	The kg St. have been made according to STAMKART's direction
St 2	Nº 2 („)	K. Ak. v. Wet.	„	„ „	„	
St 5	Nº 5 („)	Nat. lab. Utrecht	„	„ „	„	
St 6	Nº 6 („)	„ „ Gron.	„	„ „	„	
St 7	Nº 7 („)	„ „ Amst.	„	„ „	„	
P″		„ „ Delft	1872	„ „	„	
V		State Mint	1899	sphere	„	Present standard of Mint

B. GLASS WEIGHTS.

	Old name	Property of	Prepared in	Form	Surface	Remarks
G$_2$		K. Ak. v. Wet.	1856	bottle w. Hg		OUDEMANS' comparing weight
G$_1$		State Mint	1886	„ „ „		Cf. OUDEMANS l.c., p. 252

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1) Handed over to the Inspection of Weights and Measures in Holland.

The kilogrammes M, S, V, and G_1 of the State Mint had been weighed already before.

A full account of the weighings and the calculations is found in the Archives of the Committee, here only the results will be given. Under the heading "mass" it is stated in the following table how much this is greater (+) or smaller (—) than that of Pt.

1. Weights of the Committee:

	Vol. in mm^3	At temperature	Mass in 1926
I	118868	14°5	+ 1.32 mg
II	118828	12°	— 0.24 „
III	118860	14°	+ 1.59 „

2. Kilogrammes that have also been compared by OUDEMANS. The volumes have been determined by STAMKART and by OUDEMANS.

	Volume in mm^3	At temp.	Ob-server	Mass in mg		Change per year
				1886	1926	
v. Sw	123312	0°	O.	+ 0.19	+ 0.74	+ 0.01
F_1	126060	0°	O.	+ 152.36	+ 186.49	+ 0.85
Sl	119127	0°	O.	+ 40.78	+ 39.90	— 0.02
Contr	119043	0°	O.	+ 47.06	+ 46.21	— 0.02
B	122424	0°	O.	+ 0.05	+ 2.85	+ 0.07
Del	129449	0°	O.	+ 573.83	+ 716.94	+ 3.58
S					+ 59.79	(+ 2.3)1)
L_1	122553	0°	O.	— 14.66	— 12.19	+ 0.06
L_2	122347	0°	O.	+ 54.47	+ 56.58	+ 0.05
L_3	123327	0°	O.	— 40.32	— 39.60	+ 0.02
KI	122050	0°	O.	+ 77.43	+ 84.74	+ 0.18
St 1	121615	0°	St.	+ 1.14	+ 1.58	+ 0.01
St 2	120816	0°	St.	— 12.23	— 11.71	+ 0.01
St 5	120169	0°	St.	— 2.73	— 2.92	— 0.00
St 6	122710	0°	St.	— 2.05	+ 0.15	+ 0.05
St 7	120059	0°	St.	— 0.49	+ 0.37	+ 0.02
P″	121496	15°	St.	— 6.87	— 12.61	— 0.14
G_2	99805	0°	O.	+ 5.52	+ 6.53	+ 0.03

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1) The weight was re-adjusted in 1889.

3. Other kilogrammes. The volumes of them have been determined by the Committee LIPKENS etc. of 1838, by OUDEMANS, HOITSEMA, or SIERTSEMA.

	Volume in mm^3	Temp.	Observer	Mass in mg		Mass in mg			Change per year
							Before the hydr. w.	After the hydr. w.	
L_{10}	121387	15.5°	S.	1839	— 12.93 1)	1926	— 17.89	— 18.97	— 0.05
Aen	123135	15.5°	S.	1909	— 12.05 2)	1927	— 8.83	— 10.78	+ 0.18
F_2	124257	16.0°	S.			1927	— 73.69	— 76.64	
M				1902	— 8.2 3)	1925	— 5.98		+ 0.10
A	123755	0°	L.			1926	— 7.52		
C	121759	0°	L.	1839	— 1.02	1926	— 5.76		— 0.05
V	118486	0°	H.	1902	— 7.85 4)	1925	— 8.46		— 0.03
G_1	104458	0°	O.	1902	— 3.3 5)	1925	— 18.91		— 0.68

The volumes of S and M are not known. In the calculations they have been put equal to that of V.

It appears that of the very old weights some (v. Sw, Sl, Contr, L_3) have changed very little. Perhaps L_{10} and Aen may also have kept better than the values found would lead us to suppose; the losses of weight in the hydrostatic weighings indicate that the surface may have been dirty. Also STAMKART's gilt weights St 1—St 7 have kept well. It is a pity that on account of the screwed-on knob these weights are useless as standard weights. The GANDOLFI's weight M should be very constant as HOITSEMA supposed 6), finds no confirmation here.

Some weights show a remarkably great increase. This is the case in a very high degree with the weight Del of the Mint, which OUDEMANS also already observed, at the same time drawing attention to the abnormally large volume. Externally there is nothing to be perceived in this weight that would account for the continued increase, only the surface is slightly tarnished.

Slightly less great is the increase in F_1, an old weight of FORTIN. If this weight was originally (about 1800) accurate, this would also furnish a case of a progressing unaccountable increase. The change of the

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1) According to a weighing of the Committee LIPKENS etc. of 1838. Cf. OUDEMANS (1887) l.c. p. 232.

2) According to a weighing by KIST.

3) Cf. HOITSEMA, Muntverslag 1908 p. 42.

4) According to a written statement of HOITSEMA.

5) Cf. HOITSEMA, Muntverslag 1902 p. 134.

6) HOITSEMA, Muntverslag 1902 p. 116.

glass weight G_1 of the Mint might perhaps be explained by the condition of the surface, and would call for further confirmation. Also K I of the Royal Academy of Sciences, a to all appearances well preserved weight. has greatly increased.

An unexplained decrease may be observed in the Delft weight P″. This decrease, too, drew already the attention in 1886, and has continued ever since, though in a slightly less degree. It is a weight gilt in the fire, the exterior of which shows nothing that can account for the decrease.

Summarizing it may be said that many old weights, especially the gilt ones, have changed very little. The galvanically gilt St 2, St 5, St 6, St 7 are not inferior to St 1 and P″ gilt in the fire. The unaccountable great variability of some weights, however, shows the need of caution, and renders it necessary often to verify standard weights.

Physical Laboratory of the Technical University
at Delft.

Chemistry. — *Osmosis of ternary liquids. General considerations.* III. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of November 26, 1927).

1. *The diagram.*

In the last paper we saw that from the change of the concentration of one of the substances it cannot be deduced in which direction this substance diffuses through the membrane; for this reason we have called this the "apparent" osmosis. In order to ascertain this direction we shall also have to consider liquids in which the concentration of one or two of the substances is negative; consequently we shall begin by briefly indicating by which points they are represented.

We imagine in fig. 1 the sides of the triangle WXY prolongated infinitely; then the plane is divided into seven fields I—VII. Field I coincides with triangle WXY, the other fields are situated outside. If we represent the composition of a liquid by:

$$x \text{ quant. of } X + y \text{ quant. of } Y + (1-x-y) \text{ quant. of } W$$

then it follows: $WX = WY = 1$. We now have:

x is positive on the right side of the line WY
x „ negative „ „ left „ „ „ „ „
y „ positive above the line WX
y „ negative beneath „ „ „

For a point 1 in field I $x = +(1a)$ and $y = +(1b)$ if $(1a)$ and $(1b)$ represent the lengths of those lines. From the figure follows:

$$(1a) + (1b) + (1c) = 1$$

consequently:

$$x + y + (1c) = 1 \quad \text{or} \quad 1 - x - y = +(1c)$$

So the W-amount of liquid 1 is positive, and it is represented by $+(1c)$. Hence follows: points in field I represent liquids with positive X-, Y- and W-amounts.

For a point 2 in field II $x = +(2a)$ and $y = +(2d)$; from the figure it follows:

$$(2a) + (2d) - (2c) = 1$$

consequently:

$$x + y - (2c) = 1 \quad \text{or} \quad 1 - x - y = -(2c)$$

So the W-amount of liquid 2 is negative, and it is represented by $-(2c)$. We now find:

points in field II represent liquids with a positive X- and Y-amount but with a negative W-amount.

Later on we shall refer to the meaning of such liquids.

For a point 3 in field III $x = -(3e)$ and $y = +(3g)$; the X-amount

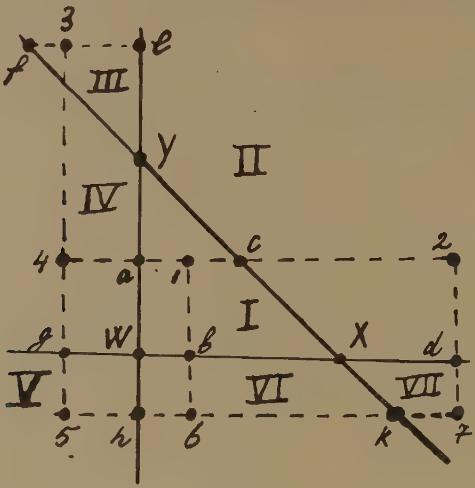

Fig. 1.

of this liquid now is negative and the Y-amount positive; it follows from the figure:

$$(3g) - (3e) - (3f) = 1$$

consequently:

$$y + x - (3f) = 1 \quad \text{or} \quad 1 - x - y = -(3f)$$

So the W-amount of liquid 3 is negative, we now find:

points in field III represent liquids with a positive Y-amount, but with negative X- and W-amounts.

If we act in a corresponding way for the points 4, 5 etc., we shall be able to represent the results in a table. In table 1 the values of x, y

TABLE 1. (fig. 1.)

Field	x	y	$1-x-y$	X	Y	W
I	$+(1a)$	$+(1b)$	$+(1c)$	+	+	+
II	$+(2a)$	$+(2d)$	$-(2c)$	+	+	—
III	$-(3c)$	$+(3g)$	$-(3f)$	—	+	—
IV	$-(4a)$	$+(4g)$	$+(4c)$	—	+	+
V	$-(5h)$	$-(5g)$	$+(5k)$	—	—	+
VI	$+(6h)$	$-(6b)$	$+(6k)$	+	—	+
VII	$+(7h)$	$-(7d)$	$-(7k)$	+	—	—

and $1-x-y$ have been indicated for the points 1—7; sub X, Y and W we find whether the amount of these substances is positive or negative.

This table shows among other things that:
the W-amount of a liquid is represented by the length of the horizontal line, which is drawn from that point up to the line XY.

The W-amount is positive in the fields I, IV, V and VI, consequently when the point is situated on the same side of the line XY as point W.

The W-amount is negative in the fields II, III and VII, consequently when the point is situated on the side of the line XY opposite to point W.

In the fields II and V the X-, Y- and W-amount have opposite signs; for this reason we shall call those fields "opposite" fields. The same is valid for the fields III and VI and also for IV and VII.

2. *The diffused and the diffusing mixture,* (*real osmosis*). *Positive and negative osmosis.*

We imagine a part of the osmosis-path of the system

$$L \mid L' \quad \ldots\ldots\ldots \quad (1)$$

to be represented in fig. 2 by the curves $p\,z\,r$ and $p'\,z'\,r'$; as e is the final liquid, these curves must terminate in point e.

Liquid L travels along path $p\,z\,r$ and liquid L' along path $p'\,z'\,r'$ in the direction of the arrows. At a certain moment t_1 we shall have the system

$$L_1 \mid L_1' \quad \ldots\ldots\ldots \quad (2)$$

and at a later time t_2 the system

$$L_2 \mid L_2' \quad \ldots\ldots\ldots \quad (3)$$

During the time t_2—t_1 a definite quantity of each of the substances has passed through the membrane; if those substances have all gone in the same direction, we, therefore, may say that a liquid of a definite composition has diffused; then the quantity of this liquid has been defined also.

If the substances do not diffuse in the same direction, we shall say notwithstanding that a liquid has passed through the membrane; then however this liquid has one or two negative concentrations; we then have a liquid like the one discussed in fig. 1 and table 1.

In both cases we shall now say that a "mixture" has diffused through the membrane; we shall call it the "diffused" mixture.

In order to find out the composition of the mixture which has diffused in the time t_2—t_1, we draw the line $a\,b$ in fig. 2 through the points 1 and 2; we imagine those points a and b at an infinite distance. We now see that L_1 can pass into L_2:

either if L_1 absorbs a mixture, which is represented by a point between 2 and b

or if L_1 gives off a mixture which is represented by a point between 1 and a.

During the osmosis, therefore, the liquid L_1 has absorbed or given off a mixture, which is situated somewhere on the infinitely prolonged curve 1 . 2 (except between the points 1 and 2 themselves).

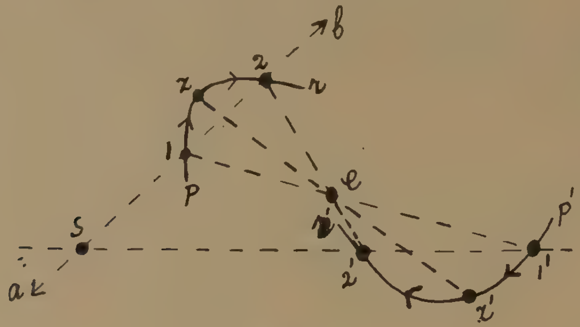

Fig. 2.

Something corresponding to this is valid for the liquid L_1'; this has passed into L_2' and has, therefore, absorbed or given off a mixture, which is situated somewhere on the infinitely prolonged curve 1′ . 2′. If we call the point of intersection of these chords s, we see:

L_1 can pass into L_2 if L_1 gives off the mixture L_s.

L_1' can pass into L_2' if L_1' absorbs the mixture L_s.

Consequently we find:

in the time $t_2 - t_1$ the mixture L_s has diffused from the left to right through the membrane.

We represent this by:

$$L_1 \mid L_1' \longrightarrow L_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The composition of this diffused mixture L_s is represented by the point of intersection of the conjugated chords 1 . 2 and 1′ . 2′.

From the position of this point s may now be deduced in which direction each of the substances has diffused through the membrane. We begin by assuming that point s is situated on the part 1 . a of the chord as has been drawn in fig. 2; as, therefore, the liquid L_1 gives off this mixture, it must go through the membrane from left to right. (Comp. scheme 4).

If point s is situated within field I (comp. fig. 1) then it represents a mixture with a positive X-, Y- and W-amount. As this mixture goes through the membrane from left to right, the substances X, Y and W must therefore also go from left to right; we represent this by:

$$\underset{\longrightarrow}{L_s} \qquad \underset{\longrightarrow}{X} \qquad \underset{\longrightarrow}{Y} \qquad \underset{\longrightarrow}{W} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If, however, point s is situated within field IV, then it represents a mixture, which has a negative X-amount, but a positive Y- and W-amount (comp. fig. 1 and table 1). Consequently a negative quantity of X, but a positive quantity of Y and W goes from left to right; the substance X, therefore, goes through the membrane from right to left and the substances Y and W from left to right. We represent this by:

$$\underset{\longrightarrow}{L_s} \qquad \underset{\longleftarrow}{X} \qquad \underset{\longrightarrow}{Y} \qquad \underset{\longrightarrow}{W} \quad \ldots\ldots \quad (6$$

If in fig. 2 we imagine the entire osmosis-path with the two chords and point s to have turned $\pm 180^\circ$ round point e, then we see that point s can also be situated in field II. It appears from fig. 1 or table 1 that the mixture then has a positive X- and Y-amount, but a negative W-amount. As this mixture is also given off by L_1 and therefore goes through the membrane towards the right side, X and Y will consequently diffuse towards the right side and W towards the left side. We then get the scheme:

$$\underset{\longrightarrow}{L_s} \qquad \underset{\longrightarrow}{X} \qquad \underset{\longrightarrow}{Y} \qquad \underset{\longleftarrow}{W} \quad \ldots\ldots \quad (7)$$

If point s is situated in one of the other fields of fig. 1 then we can ascertain in the same way as shown above the direction, in which the substances diffuse through the membrane, for each field. In scheme (8) we find those directions indicated for each of the seven fields.

$$\left.\begin{array}{cccccccc}
 & & & \multicolumn{3}{c}{L_1 \mid L_1' \longrightarrow L_s} & & \\
 & \text{I} & \text{II} & \text{III} & \text{IV} & \text{V} & \text{VI} & \text{VII} \\
X & \longrightarrow & \longrightarrow & \longleftarrow & \longleftarrow & \longleftarrow & \longrightarrow & \longrightarrow \\
Y & \longrightarrow & \longrightarrow & \longrightarrow & \longrightarrow & \longleftarrow & \longleftarrow & \longleftarrow \\
W & \longrightarrow & \longleftarrow & \longleftarrow & \longrightarrow & \longrightarrow & \longrightarrow & \longleftarrow
\end{array}\right\} \quad . \quad (8)$$

In this scheme the directions of the arrows have been deduced supposing that in fig. 2 point s is situated on the part $1 . a$ of the chord, so that liquid L_1 gives off this mixture s. If, however, point s is situated on the part $2 . b$ then liquid L_1 absorbs this mixture s. Instead of (4) we then get:

$$L_1 \mid L_1' \longleftarrow L_s \quad \ldots\ldots\ldots \quad (9)$$

We now must give the opposite direction to all arrows in scheme 8.

The diffused mixture, however, not only defines the directions in which the substances have passed through the membrane, but also the ratio in which this has taken place.

For the sake of concentration we assume e.g. that it is situated in point 4 of fig. 1; we then have (comp. also table 1):

$$x = -(4\,a) \qquad y = +(4\,g) \qquad 1 - x - y = +(4\,c).$$

The ratio in which X, Y and W diffuse through the membrane, is then given by:

$$(4\,a) : (4\,g) : (4\,c)$$

Consequently we find:

if a system has passed into an other by osmosis, then the diffused mixture is represented by the point of intersection of the two conjugated chords. From this mixture follows the direction and the ratio in which the substances have diffused. As this is no "appearance" but "reality", we call this "real osmosis" in contradistinction to the "apparent osmosis" which was discussed in the last communication.

At the time t_1 system (1) is found in the points 1 and 1′ and at the time t_2 in the points 2 and 2′ of its path; then point s represents the composition of the entire mixture that has diffused through the membrane in the time $t_2—t_1$.

We now may also put the question: what is the composition of the mixture, which passes through the membrane at any moment? For it is evident that this will be otherwise in the points 1 and 1′ than when the liquids are found in other points of their path.

If on branch 1 . 2 we imagine one more point u (and consequently on branch 1′. 2′ a point u') then the point of intersection of the chords $z\,u$ and $z'\,u'$ represents the diffused mixture, when the liquids have proceeded along the branches $z\,u$ and $z'u'$. If u draws nearer to z and u' to z' then the chords pass into the tangents in the points z and z'; the point of intersection of those tangents, therefore, represents the mixture which diffuses in an infinitely small time $d\,t$ through the membrane at the moment that the liquids are found in the points z and z' of their path. We call this the "diffusing" mixture; consequently we find:

the mixture diffusing each moment is represented by the point of intersection of two conjugated tangents of the path.

At the beginning of the osmosis, viz. when the liquids are found in 1 and 1′, this mixture is represented, therefore, by the point of intersection of the tangents in 1 and 1′; at the end of the osmosis considered, viz. if the liquids are found in 2 and 2′, by the point of intersection of the tangents in 2 and 2′.

Of course the same things, deduced above for the "diffused" mixture are valid for a "diffusing" mixture, as the only difference between both mixtures regards the duration of the osmosis; for the "diffused" mixture passes through the membrane in a finite time $t_2—t_1$, the "diffusing" in an infinitely short time $d\,t$.

If in fig. 2 we imagine that some pairs of conjugated tangents have been drawn, we see, that their points of intersection can be situated also in other fields than point s. Consequently we should not draw a conlusion with respect to the position of the diffusing mixtures from the position of the diffused mixture. This is also clear, if we take into consideration that the diffused mixture is defined only by the beginning- and terminating points of the branches 1 . 2 and 1′. 2′ which have been travelled, and that the form of those branches has no influence on this; the position of the diffusing mixtures, however, is defined by the form of those branches.

While, therefore, from the diffusing mixtures may be deduced what takes place at any moment of the osmosis, this is not always possible with the aid of the diffused mixture; we shall refer to this later on.

In order easily to distinguish the cases which may occur with the osmosis of a substance, we shall represent them again by a scheme. Again we indicate by the signs $>$ and $<$ on which side of the membrane the concentration of a substance is larger or smaller; by an arrow we indicate the direction in which this substance diffuses through the membrane.

(*a*) $\overset{<}{\longleftarrow}$ and $\overset{>}{\longrightarrow}$

If we take a definite substance e.g. X then the first scheme indicates that the X-amount on the left side of the membrane is smaller than that on the right side and that the substance X diffuses from right to left.

The second scheme indicates that the X-amount on the left side of the membrane is larger than that on the right side and that the substance diffuses from left to right.

In both cases, therefore, X diffuses from the liquid with the larger X-amount towards the liquid with the smaller X-amount; we call this a "positive" X-osmosis.

As we shall see later on in experimental cases, we can also have, however, the schemes:

(*b*) $\overset{<}{\longrightarrow}{}_{*}$ and $\overset{>}{\longleftarrow}{}_{*}$

Now the substance X diffuses from the liquid with the smaller X-amount towards that with the larger X-amount; we call this a "negative" osmosis.

In the preceeding paper we have placed an * with the arrows, which indicate an anormal change of a concentration; now we do this also with the arrows which indicate a negative osmosis.

In our last communication we have discussed the apparent osmosis of a system

$$L \mid L' \qquad \ldots\ldots\ldots \qquad (10)$$

which goes along its path 1 e 1′ in fig. 1 (Comm. II); we find this in table 10 (Comm. II); now we shall deduce the real osmosis of this system.

In this figure we imagine somewhere on the path $1 . e$ a liquid u; the conjugated liquid must then be situated on path $1' . e$; the diffusing mixture is then represented by the point of intersection u'' of the tangents in u and u'. If u proceeds along the path $1 . e$ and consequently u' along the path $1' . e$ then u'' will proceed along a path $1'' e''$ which we shall call the "path of the diffusing mixture". We shall represent this in fig. 3. In this we imagine the path $1 . e . 1'$ of fig. 1 (Comm. II) drawn inside the triangle WXY, in which, however, the letters W, X and Y have been omitted; in fig. 3 only the point a of this path is indicated.

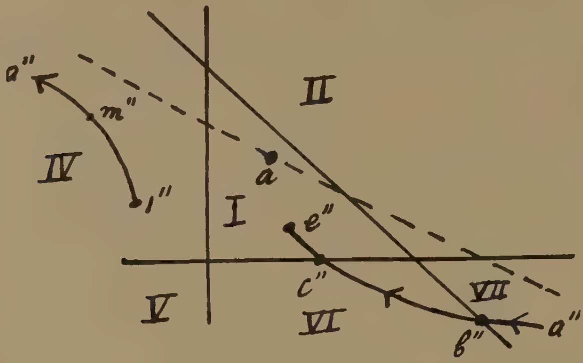

Fig. 3.

When liquid u is in point 1 (and consequently u' in $1'$), then the diffusing mixture u'' is situated in field IV; it is represented in fig. 3 by $1''$. When liquid u is in point m, then u'' too is still situated in field IV; it is represented in fig. 3 by m''.

Matters change, however, when liquid u is in point 3 (and consequently u' in $3'$). For the tangent in point 3 is parallel to side XY of the triangle; its point of intersection with the tangent in $3'$ which was not drawn, is situated, therefore, either in field I or in field VI. From this it appears that between the points m and 3 a point a is situated, which has the following property: the tangent in point a and that in point a', which was not drawn, run parallel. The line drawn through point a in fig. 3 represents this tangent in a; the point of intersection of the two tangents is situated at infinite distance; it is represented in in fig. 3 by a'' which we may imagine as well in field IV as in field VII at infinite distance. Consequently we find:

if liquid u proceeds along part $1 . 2 . m . a$ of its path, then u'' proceeds along path $1'' a''$, situated in field IV, of which a'' is situated at infinite distance.

If liquid u proceeds further along the path $a\, e$, then u'' proceeds along a path $a'' e''$ (fig. 3) which now starts from point a'', which is situated at infinite distance in field VII. We assume that this path intersects the sides XY and WX in the points b'' and c''. Then two points b and c in fig. 1 (Comm. II), the first of which is situated between a and 3 and the second between 3 and 4, go with those points of intersection. Consequently we find:

if liquid u proceeds along path $1.e$ then liquid u' proceeds along path $1'.e$ and u'' along the path of the diffusing mixture, consisting of the branches $1''a''$ and $a''e''$.

Consequently we find also:

the diffusing mixture of a liquid on

$1.2.m.a$ is situated in field IV
ab ,, ,, ,, ,, VII
$b3c$,, ,, ,, ,, VI
$c4e$,, ,, ,, ,, I

Hence we may deduce in which direction the diffusing mixture and each of the three substances diffuse through the membrane; we find this in scheme (11).

$$\left.\begin{array}{llcccc} & & L_s & X & Y & W \\ 1.2m.a & \mathrm{IV} & \longrightarrow & \longleftarrow & \longrightarrow & \longrightarrow \\ ab & \mathrm{VII} & \longleftarrow & ,, & ,, & ,, \\ b3c & \mathrm{VI} & ,, & ,, & ,, & \longleftarrow \\ c4e & \mathrm{I} & ,, & ,, & \longleftarrow & ,, \end{array}\right\} \quad . \; . \; . \quad (11)$$

For if liquid u is on $1.a$, then u'' is situated in field IV; therefore, u'' has a negative X-amount, but positive Y- and W-amount (compare table 1 or fig. 1). As during the osmosis liquid u moves away from u'', liquid u, therefore, gives off the diffusing mixture. Hence it follows, that:

during the osmosis the liquid absorbs X and gives off Y and W.

If liquid u is on ae and, therefore, u'' on $a''e''$, then during the osmosis u will approach u''; consequently liquid u absorbs the diffusing mixture; therefore, this passes towards the left through the membrane.

If u'' is situated on $a''b''$, consequently in field VII, then it has a positive X-amount, but negative Y- and W-amounts; the liquid u, therefore, absorbs X and gives off Y and W.

If, however, u'' is situated on $b''c''$, consequently in field VI, then it has positive X- and W-amounts, but a negative Y-amount; now the liquid u absorbs X and W and it gives off Y.

If, to conclude, u'' is situated on $c''e''$, consequently in field I, then the X-, Y- and W-amounts are positive; therefore, the liquid u absorbs X, Y and W.

As has already been said above, all this may be found in scheme (11).

From scheme 11 we can now see in which direction each of the substances diffuses at any moment through the membrane. We get, however, a better and completer survey if, besides the "real" we also consider the "apparent" osmosis; we find the latter in scheme 10 of the last paper.

We begin by imagining liquid z on branch 1.2 (fig. 1, Comm. II). With the aid of scheme (11) of the present and of scheme 10 of the preceeding paper, we now find:

$$\begin{array}{llcccc} & & L_s & X & Y & W \\ 1.2 & \mathrm{IV} & \longrightarrow & \underset{\longleftarrow}{\uparrow<\downarrow} & \underset{\longrightarrow}{{}^*\uparrow>\uparrow} & \underset{\longrightarrow}{\downarrow>\uparrow} \end{array} \quad . \quad . \quad . \quad . \qquad (12)$$

In this we see: on which side of the membrane the concentration of a substance is greatest (smallest), how those concentrations change, and in which direction the substances and the diffusing mixture go through the membrane. We see that there is only one anormal change and that all substances diffuse in positive direction, viz. from the liquid with the greater concentration towards the liquid with the smaller concentration.

For liquids of branch 2 . m we find:

$$\begin{array}{llcccc} & & L_s & X & Y & W \\ 2.m & \mathrm{IV} & \longrightarrow & \underset{\longleftarrow}{\uparrow<\downarrow} & \underset{\longrightarrow}{{}^*\uparrow>\uparrow} & \underset{\longrightarrow{}^*}{{}^*\downarrow<\uparrow^*} \end{array} \quad . \quad . \quad . \qquad (13)$$

There are now three anormal changes viz. that of substance Y on the left side and those of the substance W on both sides of the membrane. Now there is also a negative osmosis; for substance W diffuses from the liquid with the smallest W-amount towards that with the largest W-amount.

It would carry us too far if we were here to write down the schemes for all branches; we shall only add that for the branch c . 4; we find:

$$\begin{array}{llcccc} & & L_s & X & Y & W \\ c.4 & \mathrm{I} & \longleftarrow & \underset{\longleftarrow}{\uparrow<\downarrow} & \underset{\longleftarrow{}^*}{\downarrow>\uparrow} & \underset{\longleftarrow}{\uparrow<\uparrow^*} \end{array} \quad . \quad . \quad . \qquad (14)$$

There is now one anormal change viz. that of substance W on the right side of the membrane and one negative osmosis viz. that of substance Y.

In the same way as above we can deduce also the schemes for the other branches of the osmosis-path; if we unite them in a single scheme, we can learn from it what occurs at any moment of the osmosis.

In making these deductions we have used the "diffusing" mixture and not the "diffused"; for we have already seen above that the latter does not always allow us to conclude with certainty what is happening. As in the experimental part we yet shall often have the latter, we are going to add a brief illustration of this.

In fig. 1 (Comm. II) we imagine the chords m . 3 and m'. $3'$; their point of intersection is situated in field IV, so that the diffused mixture has a negative X-amount, but positive Y- and W-amounts. As liquid m gives off this mixture, we get the following scheme:

$$m\,a\,b\,3 \quad \text{IV} \quad \overset{X}{\longleftarrow} \quad \overset{Y}{\longrightarrow} \quad \overset{W}{\longrightarrow} \quad \ldots\ldots \quad (15)$$

in which only the real osmosis of the three substances is indicated. Hence we now may conclude:

during the osmosis on branch $m\,a\,b\,3$ more X has diffused towards the left side than towards the right side and more Y and W towards the right side than towards the left side.

From this follows:

substance X will have diffused towards the left side certainly on some part of branch $m\,a\,b\,3$ and the substances Y and W will have diffused towards the right side certainly on some part of this branch.

From this, however, we may not conclude that this is the case on the whole of branch $m\,a\,b\,3$; this may be the case, but it may also be otherwise.

For if we compare schemes (15) and (11), we see that the direction of the arrows is the same in both schemes for the part $m\,a$ and $a\,b$; this is, however, no more the case for part $b\,3$; the arrow which indicates the direction of substance W in (15) runs opposite to that in (11). Consequently scheme (15) is valid for the substances X and Y on the whole of branch $m\,a\,b\,3$, but only on part $m\,a\,b$ as regards substance W.

Also with respect to the direction in which the mixtures pass through the membrane, similar deviations may occur.

Of course, there are also branches on which the scheme, deduced from the diffused mixture is valid for each substance on the whole branch; this is e.g. the case on the branches $1\,.\,2$ and $2\,.\,m$. It is clear that in general this will happen the more, the smaller the branches under consideration; then the diffused mixture approaches the diffusing mixture more closely.

(*To be continued*).

Leiden, Lab. of inorg. Chemistry.

Chemistry. — *Osmosis of ternary liquids. General considerations* IV.
By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of December 17, 1927).

The diffusing mixture and the diffusing liquid.

In communication III we have seen: if a liquid u proceeds along its osmosis-path $1.e$ (fig. 1, Comm. II), then the other liquid u' proceeds along the path $1'.e$ and the diffusing mixture along a path, consisting of the two branches $1''a''$ and $a''e''$ (fig. 3, Comm. III). During the osmosis both liquids and the diffusing mixture change their compositions continuously; now we shall see in what way we may deduce the change of their quantities.

If at a moment t_1 there is n_1 quantities of L_1 on the left side of the membrane and on the right side n_1' quantities of L_1', we represent the system by:

$$n_1 \times L_1 \;\vdots\; n_1' \times L_1' \quad \ldots\ldots\ldots \quad (1)$$

At a moment t_2 this has passed into:

$$(n_1 - \triangle n) \times L_2 \;\vdots\; (n_1' + \triangle n) \times L_2' \quad \ldots\ldots \quad (2)$$

For the sake of concentration we imagine those liquids to be represented by the points 1, 1′, 2 and 2′ of fig. 2 (Comm. III). Consequently we have assumed, as it appears from (1) and (2), that $\triangle n$ quantities of the mixture s have diffused from left to right in the time $\triangle t = t_2 - t_1$.

If we consider the liquids on the left side of the membrane, we see that n_1 quantities of L_1 pass into $(n_1 - \triangle n)$ quantities of L_2 by giving $\triangle n$ quantities of L_s. We may write, therefore:

n_1 quant. of $L_1 - \triangle n$ quant. of $L_s = (n_1 - \triangle n)$ quant. of L_2.

We can also substitute for this:

n_1 quant. of $L_1 = \triangle n$ quant. of $L_s + (n_1 - \triangle n)$ quant. of L_2.

Consequently we can get the liquid L_1 by bringing together L_s and L_2 in the ratio $\triangle n : (n_1 - \triangle n)$. From this follows that point 1 must divide the line $s.2$ into the parts $1.s$ and 1.2 which satisfy:

$$1.s : 1.2 = (n_1 - \triangle n) : \triangle n \quad \ldots\ldots\ldots \quad (3)$$

From this it follows:

$$\triangle n = \frac{1.2}{1.s + 1.2} \times n_1 = \frac{1.2}{s.2} \times n_1 = a\, n_1 \quad \ldots\ldots \quad (4)$$

In order to given this a different form, we represent the composition of the mixture s by:

$$x_0 \text{ quant. of } X + y_0 \text{ quant. of } Y + (1 - x_0 - y_0) \text{ quant. of } W.$$

In order to represent the liquids 1 and 2, we substitute the index 0 by 1 and 2. In fig. 2 (Comm. III) we now imagine the sides WX and WY to be drawn and the coordinates of the points 1, 2 and 3.

Then we find:

$$1.2 : s.2 = (x_2 - x_1) : (x_2 - x_0) = (y_2 - y_1) : (y_2 - y_0).$$

From this follows:

$$\triangle n = a\, n_1 = \frac{1.2}{s.2} \times n_1 = \frac{x_2 - x_1}{x_2 - x_0} \times n_1 = \frac{y_2 - y_1}{y_2 - y_0} \times n_1 \quad . \quad . \quad (5)$$

So if we know the quantity n_1 of the liquid, which at the moment t_1 is on the left side of the membrane, we know also the quantity $\triangle n$, which has diffused through the membrane in the time $\triangle t = t_2 - t_1$. If $\triangle n$ is positive, then this quantity has diffused towards the right side, if $\triangle n$ is negative, then this quantity has diffused towards the left side.

It also follows from this how much of each of the substances has diffused through the membrane in this time $\triangle t$. We find:

$$\left.\begin{array}{ll} x_0 \triangle n = \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1\, x_0 = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1\, x_0 & \text{quant. of } X \\[2ex] y_0 \triangle n = \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1\, y_0 = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1\, y_0 & \text{quant. of } Y \\[2ex] \text{and } \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1 (1 - x_0 - y_0) = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1 (1 - x_0 - y_0) & \text{quant. of } W \end{array}\right\} \quad . \quad (6)$$

A positive quantity has diffused towards the right side, a negative quantity towards the left side.

From (5) we can among other things deduce the following: if the diffused mixture is situated at infinite distance, then the quantity $\triangle n$, which has diffused in the time $\triangle t = t_2 - t_1$ through the membrane, is zero.

This becomes clear at once if we increase x_0 (or y_0) in (5) infinitely.

We must not think now, however, that in the time $\triangle t$ nothing has gone through the membrane. If in (6) e.g. x_0 and y_0 are taken infinitely large, we find:

$$\left.\begin{array}{c} x_0 \triangle n = (x_1 - x_2)\, n_1 \qquad y_0 \triangle n = (y_1 - y_2)\, n_1 \\ (1 - x_0 - y_0) \triangle n = (x_2 + y_2 - x_1 - y_1)\, n_1 \end{array}\right\} \quad . \quad . \quad (7)$$

which can also be very simply deduced in other ways. It now appears from (7) that in the time $\triangle t$ substances have indeed gone through the membrane, but that their total quantity is zero. Consequently we find:

if in the time $\triangle t$ a quantity p of the one substance and a quantity q of the other substance diffuses towards the right (or left) side, then in the same time a quantity $p+q$ of the third substance goes in opposite direction.

Consequently we have at the moment t_2 the same quantity of liquid on both sides of the membrane as at the moment t_1; in general, however, the volume will be different at the moments t_1 and t_2: the liquids have namely an other composition at the moments t_2 and t_1 respectively.

In order to find out what passes through the membrane in the infinitely small time dt, we imagine the points 2 and 2′ in the immediate vicinity of 1 and 1′; then we have:

$$x_2 = x_1 + dx_1 \qquad y_2 = y_1 + dy_1$$

If we substitute these in (5) and omit the index 1, it follows:

$$dn = a\,n = \frac{dx}{x - x_0} \times n = \frac{dy}{y - y_0} \times n \quad . \; . \; . \; . \; . \quad (8)$$

The infinitely small quantity dn which passes through the membrane in the infinitely small time dt is, therefore, defined by (8). Instead of (6) we find:

$$\left.\begin{array}{lr} x_0\,dn = \dfrac{dx}{x - x_0} \times n\,x_0 = \dfrac{dy}{y - y_0} \times n\,x_0 & \text{quant. of } X \\[2ex] y_0\,dn = \dfrac{dx}{x - x_0} \times n\,y_0 = \dfrac{dx}{y - y_0} \times n\,y_0 & \text{quant. of } Y \\[2ex] \text{and } \dfrac{dx}{x - x_0} \times n\,(1 - x_0 - y_0) = \dfrac{dy}{y - y_0} \times n\,(1 - x_0 - y_0) & \text{quant. of } W \end{array}\right\} \; . \quad (9)$$

The infinitely small quantities of the substance, which pass through the membrane in the time dt, are, therefore, defined by (9). If we take x_0 and y_0 infinitely large here, we find the same things as we have deduced above for the diffused mixture.

Consequently we may say:

If two conjugated tangents (or chords) of the osmosis-path run parallel and the diffusing (or diffused) mixture is situated, therefore, at infinite distance, then two of the substances diffuse in one direction through the membrane and a corresponding quantity of the third substance in the opposite direction.

In communication III we have seen: if a liquid u passes along the path $1 . e$ of fig. 1 (Comm. II), then the diffusing mixture u'' proceeds along a path, consisting of the branches $1''a''$ and $a''e''$ of fig. 3 (Comm. III). In scheme 11 (Comm. III) we find the direction indicated in which the diffusing mixture and each of the substances pass through the membrane. If we add to this what we are going to discuss further as regards the points a, b and c, we get scheme (10).

$$\left.\begin{array}{llcccc} & & L_s & X & Y & W \\ 1.2.ma & \mathrm{IV} & \longrightarrow & \longleftarrow & \longrightarrow & \longrightarrow \\ a & \infty & 0 & '' & '' & '' \\ ab & \mathrm{VII} & \longleftarrow & '' & '' & '' \\ b & XY & '' & '' & '' & 0 \\ b\,3\,c & \mathrm{VI} & '' & '' & '' & \longleftarrow \\ c & XW & '' & '' & 0 & '' \\ c\,4\,e & \mathrm{I} & '' & '' & \longleftarrow & '' \end{array}\right\} \quad . \quad (10)$$

If liquid u is in point a of its path, then u'' is, therefore, in point a'' which is situated at infinite distance; so the quantity of the diffusing mixture is zero; this is indicated in scheme (10) by the symbol ∞ and the figure 0. At this moment the substances Y and W diffuse towards the right side and a corresponding quantity of X towards the left side.

If liquid u is in point c, then u'' is in point c'' on side WX (fig. 3. Comm. III); the diffusing mixture, therefore, only contains the substances W and X so that no Y diffuses; this has been indicated in scheme (10) by the figure 0. It is apparent from this scheme: if liquid u travels along its path, then Y diffuses:

towards the right side, when u is situated between 1 and c
towards the left side, when u is situated between c and e

but in point c, Y does not diffuse.

If liquid u is in point b and, therefore, u'' in point b'' on side XY, then only the substances X and Y will diffuse; substance W does not diffuse. It now appears from scheme (10) if liquid u travels along its path, then W diffuses:

towards the right side, if u is situated between 1 and b,
towards the left side, if u is situated between b and e,

but in point b the substance W does not diffuse.

We shall now consider the osmotic systems:

$$L_2 \mid L_2' \qquad L_b \mid L_b' \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

of fig. 1 (Comm. II). In the former, which we have already discussed in our previous communications, both liquids have the same amount of W. It now appears from scheme (10):

in the first of these systems the substance W diffuses through the membrane, although both liquids have the same amount of W;

in the second system no W diffuses through the membrane, although both liquids have a different amount of W.

In order to represent the concentrations of the liquids during the osmosis, we have in communication II in the figs. 2, 3 and 4 drawn the time on the horizontal axis and on the vertical axis in fig. 2 the X-amount, in fig. 3 the Y-amount and in fig. 4 the W-amount.

We now can do the same for the diffusing mixture and besides indicate at the same time also in which direction the substance passes through the membrane. The axis $O t$ (fig. 1) namely divides the diagram into two parts; we shall draw the amount in the higher part (in which the arrow →) when the substance diffuses towards the right side, and in the lower part (in which the arrow ←) when the substance diffuses towards the left side.

We shall begin by considering the Y-amount. If liquid u passes along the part $1 . a$ of its path in fig. 1 (Comm. II), then the diffusing mixture u'' passes along the path $1'' a''$ of fig. 3 (Comm. III). It appears from scheme (10) that the substance Y diffuses towards the right side in all points of this branch; consequently in fig. 1 we must draw the whole of branch $1'' a''$ above the axis $O t$. It appears from fig. 3 (Comm. III)

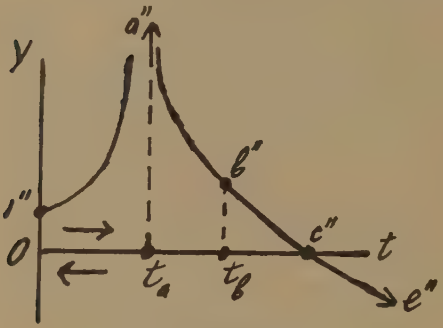

Fig. 1.

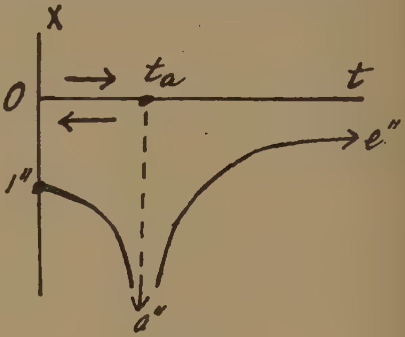

Fig. 2.

that the Y-amount increases starting from point $1''$ till in a'' where it becomes infinitely large. Therefore, in fig. 1 this branch must start from a point $1''$ on the Y-axis towards a point a'' which is situated at infinite distance on the line which goes through point t_a and runs parallel to the Y-axis.

When liquid u passes along the part $a\, b\, c\, e$ of its path, then u'' must pass along the branch $a'' b'' c'' e''$ of fig. 3 (Comm. III). It appears from scheme (10) that the substance Y diffuses towards the right side on part $a'' c''$ and towards the left side on part $c'' e''$; consequently in fig. 1 the part $a'' c''$ must be situated above the axis $O t$ and part $c'' e''$ below that axis.

As the final liquid e, however, is not reached, until after an infinitely long time, we must, therefore, imagine e'' at infinite distance.

Consequently we see in fig. 1 not only the same in scheme (10) namely the direction in which the substance Y passes through the membrane at any moment, but also in what manner the Y-amount changes continually, If we imagine these curves of fig. 1 drawn also in fig. 3 (Comm. II) then, this figure will represent all changes, occurring during the osmosis in both liquids and in the diffusing mixture.

It is clear now that we can represent the W-amount also by two curves; we then find a similar diagram as fig. 1; the curve $a''e''$, however, now intersects the axis Ot in the point t_b, so that the part $b''\,c''\,e''$ is now situated below the axis Ot.

The X-amount is represented in fig. 2. Herein we also find two curves, which are both situated, however, below the axis Ot, as, during the total osmosis the substance X diffuses towards the left side.

We assume that in a time dt

α quantities of X diffuse towards the left side and β quantities of $Y + \gamma$ quantities of W towards the right side; α, β and γ are infinitely small and positive.

Consequently we may say that $(-\alpha + \beta + \gamma)$ quantities of the diffusing mixture have passed through the membrane towards the right side in the time dt. Of course we may say also that $(\alpha - \beta - \gamma)$ quantities of this mixture go towards the left side.

If, however, we only pay attention to the quantity, passing through the membrane, no matter whether the substances diffuse towards the right or towards the left side, then during this time dt

$$(\alpha + \beta + \gamma) \text{ quantities}$$

of substance namely $X + Y + W$ pass through the membrane in all. We then may say that $(\alpha + \beta + \gamma)$ quantities of a liquid of the composition:

$$\frac{\alpha}{\alpha+\beta+\gamma} \text{ quant. of } X + \frac{\beta}{\alpha+\beta+\gamma} \text{ quant. of } Y + \frac{\gamma}{\alpha+\beta+\gamma} \text{ quant. of } W$$

pass through the membrane.

We shall call this the "diffusing liquid".

Consequently there is a difference between the diffusing mixture and the diffusing liquid. The first, namely, indicates the composition of that which passes through the membrane, if we take into consideration not only the quantities but also the direction of the diffusion. In it the concentrations can have all values varying between $+\infty$ and $-\infty$, if only their sum be 1. The diffusing liquid, however, indicates the composition of that which passes through the membrane, if we do not take into consideration the direction of the diffusion, but if we add the diffusing quantities, no matter in which direction they pass through the membrane. Consequently the concentrations are all positive and smaller than 1.

Therefore, the diffusing liquid is a real liquid, namely a liquid which we can compose of the three liquids.

This is also the case with the diffusing mixture, if this is situated in field I (consequently within triangle WXY). If it is situated, however, in one of the other fields, so that one or two of the concentrations are negative, then it is an imaginary liquid, namely a liquid which cannot exist in reality. For this reason we have called it "mixture" instead of liquid.

If we know the quantity dn and the composition:

$$x_0 \text{ quant. of } X + y_0 \text{ quant. of } Y + (1 - x_0 - y_0) \text{ quant. of } W.$$

of the mixture, which diffuses through the membrane in the time dt, then we can deduce from this the quantity and the composition of the diffusing liquid. If e.g. the mixture is situated in field IV then x_0 is negative; y_0 and $1-x_0-y_0$ are positive. We now put $x_0 = -p$ and $y_0 = q$ so that p and q are positive. Then the mixture becomes:

$$-p \text{ quant. of } X + q \text{ quant. of } Y + (1 + p - q) \text{ quant. of } W.$$

In the time dt, therefore, $p \,.\, dn$ quantities of X go through the membrane in the one direction and $q\, dn$ quantities of $Y + (1 + p - q)$ quant. of W go in opposite direction through the membrane. Consequently:

$$p\,.\,dn + q\,.\,dn + (1 + p - q)\, dn = (1 + 2\,p)\, dn$$

quantities of liquid pass through the membrane in all; the composition of this liquid is:

$$\frac{p}{1+2p} \text{ quant. of } X + \frac{q}{1+2p} \text{ quant. of } Y + \frac{1+p-q}{1+2p} \text{ quant. of } W.$$

If the mixture is situated in field VII, then y_0 and $1 - x_0 - y_0$ are negative. We now put $x_0 = p > 1$ and $y_0 = -q$. Consequently the mixture has the composition:

$$p \text{ quant. of } X - q \text{ quant. of } Y - (p - q - 1) \text{ quant. of } W.$$

We now find that $(2\,p - 1)\, dn$ quantities of liquid of the composition:

$$\frac{p}{2\,p-1} \text{ quant. of } X + \frac{q}{2\,p-1} \text{ quant. of } Y + \frac{p-q-1}{2\,p-1} \text{ quant. of } W$$

pass through the membrane.

If the mixture is situated in field VI then only y_0 is negative. We now put $x_0 = p < 1$ and $y_0 = -q$. Then the mixture has the composition:

$$p \text{ quant. of } X - q \text{ quant. of } Y + (1 - p + q) \text{ quant. of } W.$$

It follows from this that $(1 + 2\,q)\, dn$ quantities of liquid of the composition:

$$\frac{p}{1+2q} \text{ quant. of } X + \frac{q}{1+2q} \text{ quant. of } Y + \frac{1-p+q}{1+2q} \text{ quant. of } W$$

pass through the membrane.

In a corresponding way we find the quantity and composition of the diffussing liquid, when the diffusing mixture is situated in one of the other fields.

What has been discussed above is of course also valid for the diffused mixture and the diffused liquid.

If liquid u passes along its path $1 \, . \, e$ of fig. 1 (Comm. II), then the diffusing mixture u'' passes along the branches $1''a''$ and $a''e''$ of fig. 3 (Comm. III); the X-, Y- and W-amount of this mixture u'' is represented in the figures 1 and 2. In a corresponding way we can also represent the diffusing liquid.

We now shall unite the three curves in one diagram (fig. 3); in order not to make the figure too large, however, we are now going to use only the higher part. In order yet to indicate in which direction a substance passes through the membrane, we shall draw that part of the curve, on which the substance diffuses towards the right side, in full, but we shall dot the part on which the substance diffuses towards the left side.

In fig. 3 these directions are represented by an arrow fully drawn and by a dotted arrow.

As all concentrations of the diffusing liquid are now situated between 0 and 1, the curve in fig. 3 will have quite another form from those in figs. 1 and 2.

In fig. 3 the X-amount is represented by the curve, near which the letter X has been put. The starting-point $1''$ is of course situated on the axis OC and the final-point e'' at infinite distance. As the substance X diffuses towards the left side during all the osmosis, this curve has been dotted.

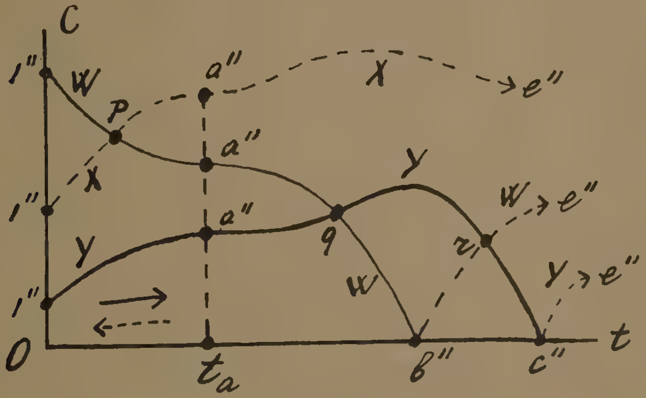

Fig. 3.

The Y-amount is represented by the curve near which the letter Y has been put. We see in scheme (10) that the Y-amount of the diffusing mixture, and consequently also that of the diffusing liquid, is zero in point c; consequently the curve must at the moment t_c come in the point c'' on the axis Ot. As on the part $1''c''$ the substance Y diffuses towards the right side and on $c''e''$ towards the left side (comp. scheme

10), the first part, therefore, has been drawn in full and the second part has been dotted.

The W-amount is represented by the curve near which the letter W has been put. It appears from scheme (10) that at the moment t_b it must come in a point b'' of the axis Ot and that the part $1''b''$ should be drawn in full and the part $b''e''$ must be dotted.

Although from a theoretical point of view little can be said as yet as to the shapes etc. of those curves; we may yet deduce a few properties.

In the first place it is clear that we always know one of those curves, when the other two are known. Somewhere on the axis Ot we imagine a point z; the perpendicular in z intersects each of the three curves in a point, we shall call z''. As each of these lines zz'' represents a concentration and as the sum of the three concentrations is 1, the sum of these three lines zz'' must, therefore, always be 1. The reader will probably not object that in drawing this sketch-figure we have not paid sufficient attention to this.

Previously we have already deduced that in point a'' the substances Y and W diffuse towards the right side and a corresponding quantity of X towards the left side (compare also scheme 10). Consequently in fig. 3 the longest line $t_a\,a''$ must, therefore, be as long as the sum of bot the other lines $t_a\,a''$; consequently it is $^1/_2$.

We can show besides that the curves have a horizontal tangent in a''.

The X- and W-curves intersect one another in point p; consequently at that moment as much X as W passes through the membrane; the X goes towards the left side and the W towards the right side.

The Y- and W-curves intersect one another in the points q and r. Consequently in q as much Y as W passes through the membrane towards the right side; in r as much Y goes towards the right side as W towards the left side.

These points of intersection correspond with definite points of fig. 3 (Comm. III). We can easily deduce:

in fig. 3 (Comm. III) point p is the point of intersection of branch $1''a''$ with the horizontal line, which is drawn through point Y;

point q is the point of intersection of branch $a''e''$ with the bisectrix of angle WXY;

point r is the point of intersection of branch $a''e''$ with the vertical line, which passes through point X.

(To be continued).

Leiden, Lab. of inorganic Chemistry.

Physics. — *Penetrating Radiation.* By J. CLAY. (Communicated by Prof. W. J. DE HAAS.)

(Communicated at the meeting of December 17, 1927).

In the following pages the results are communicated of measurements concerning the penetrating (ultra-gamma) rays during the months of February—July 1927 at Bandoeng Java Lat. 6° 45′ S, Long. 107° 16′ E. made at an altitude of 760 meters above the sea-level, and further of measurements at 3024 meters on a mountain-summit and till an altitude of 4300 meters in an aeroplane. The end of these measurements was to ascertain the intensity of the penetrating rays, to measure the absorption of the rays in lead and to trace whether a daily variation exists. Further at the same time the ionisation was measured due to the radio-activity of the ground and of the atmosphere.

§ 1. The two apparatus used for the research were according to KOLHÖRSTER's model made by GÜNTHER and TEGETMEYER. We shall call the two apparatus *A* and *B*. The capacity of *A* is 0.51 cms and that of *B* is 0.61 cms; the sensitiveness of *A* was 2 volts per scale-division and the maximal tension which could be read, was 350 volts; for *B* this amounted respectively to 3 volts and 480 volts. Either volume was 4170 cc. The walls of the two apparatus had a thickness of 3 mms of zinc; their inner surfaces were electrolitically covered with zinc in order to leave the slightest possible residual ionisation in the apparatus due to the radio-active infection of the material.

Initially the measurements were made in the laboratory built of stone up to 4 meters, the rooms of which are covered with eternite, while the roof consists of but a thin layer of iron-wood. However after it had appeared that in the building the ionisation in the electrometers was about 1 I (1 I = 1 ion per cc per sec.) more than in the open field outside the laboratory, all measurements were made out of doors under a small wooden shed of about 6 meters square. As the variation in temperature amounts to at most 12° C. at that place by day and in the night, this was by no means an objection for the measurements, seeing it appeared that the readings of the two apparatus in a thermostat at 30° C. variation in temperature under ionising influence of 1 mgr. of radium at 2 meters, distance did not record any difference at all. Besides it appeared with these measurements that the decrease of volts per sec. for tensions above 100 volts remained constant.

The ionisation due to the presence of 1 mgr. of radium at a distance of

2 meters gave an amount of 166 I fir apparatus *A* and for apparatus *B* of 160 I, i.e. EVE's figure for *A* is 6.6 . 10^9 ions cm^{-1} gr^{-1} sec.$^{-1}$ and for *B* 6.4 . 10^9 ions.

§ 2. *Earth-radiation.* For a determination of the ionisation due to the gamma-rays of the earth's surface, first one of the electrometers was placed on the earth and the ionisation measured, next on a sheet of lead of a thickness of 10 cms and surrounded by lead in such a way, that no gamma-rays of the earth could reach the apparatus. With electrometer *A* we found 6.99 I on the earth and 5.55 I on lead, with electrometer *B* 5.78 I and 4.38 I. Accordingly for the former the earth-radiation yielded 1.44 I and for the latter 1.40 I. Seeing this radiation had penetrated 3 mms of zinc, the amount for the earth-radiation directly above the surface of the earth in the open air may be fixed at 1.55 I.

The values of the ionisation on the surface of the earth were obtained from an average of 7 values with an average deviation of respectively 0.17 and 0.07 I, those on the lead for *A* from 9 values with an average deviation of 0.15 I and for *B* from 12 values with an average deviation of 0.07 I.

§ 3. *Atmospheric radiation.* The ionisation due to the emanation in the atmosphere could be neglected. In due correspondence with a former determination of the amount of emanation [1]), I found in new determinations according to the condensation-method by liquid air, that the value lies between 10^{-18} and 10^{-19} CURIE, which causes an ionisation in the electrometers of at most 0.01 I.

§ 4. *Residual rays.* In order to measure the residual radiation of the apparatus, they were surrounded on all sides by a lead-armouring of a thickness of 48 cms. It appeared that in this armouring the residual radiation was 4.28 I for *A* and 3.03 I for *B*. From this it follows, that the penetrating radiation as far as it is absorbed by 48 cms of lead, is 1.27 I according to apparatus *A* and 1.35 I according to *B*, two values, which when we bear in mind that capacity and sensitiveness of the two apparatus differ, correspond beautifully.

From this it follows that the two ionising factors in the open air must together amount to about 3 I. Seeing that prolonged registering has taught us, that the number of small ions, present in the atmosphere amounts to ca 600, it follows for the constant factor of decay (Verschwindungskonstante) according to SCHWEIDLER [2]), in case of equilibrium: $\beta' = \frac{q}{n} = \frac{3}{600} = 5.10^{-3}$.

For this figure SCHWEIDLER gives for INNSBRÜCK: 22 . 10^{-3} and POWER [3]) for MINNESOTA, U. S.: 6.1 . 10^{-3}.

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[1]) Proc. Roy. Acad. Amsterdam **28** p. 431 1925.

[2]) E. SCHWEIDLER, Wiener Ber. **133**, p. 23, 1924.

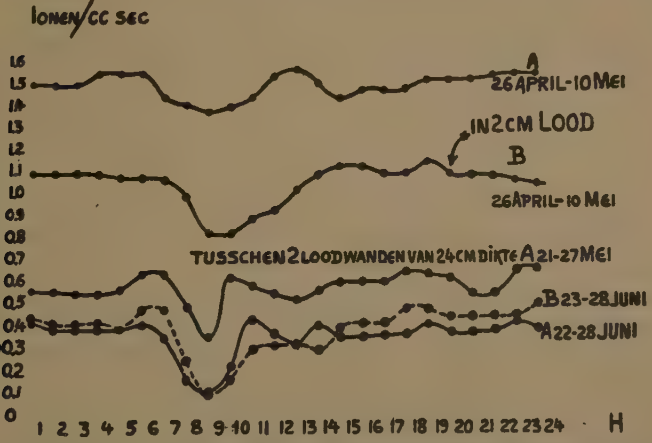
[3]) A. D. POWER, Journal Franklin Inst. **196**, p. 327, 1923.

This proves that the result obtained here, is reliable.

Now it should be at once observed, that identical values are not always found for the intensity of the residual radiation. Owing to the breaking of the tube with hygroscopic substance of the apparatus *A* this apparatus was open for a short time and after that we found 4.87 I for the radiation within a lead-armouring of a thickness of 48 cms. Further for apparatus *B* after the test for temperature-coefficient in which some change of air may have occurred, 3.44 I was found as the value within 48 cms of lead. This change was taken into account in all subsequent measurements.

§ 5. *Variation of the radiation-intensity.* In order to trace whether a daily variation existed, two series of measurements were made. Apparatus *A* was mounted on a layer of 10 cms of lead, surrounded on all sides by a layer of 12 cms of lead, so that the rays of the earth could not reach the apparatus. The apparatus *B* was mounted in a similar way, but surrounded on all sides by an additional layer of 2 cms of lead. The reduction of the charge was measured every 3 to 4 hours and during the latter part of the night usually during a period of 6 to 7 hours. It had already appeared from measurings during a shorter period, that on the whole the ionisation remains very constant, except during the morning-hours from 7 to 9 o'clock.

The averages were taken from the observations during a fortnight between April 13 and May 10 and from these averages we derive the two



Ionen/cc sec = Ions/cc sec; 26 April—10 Mei = April 26—May 10; in 2 cm lood = in 2 cms of lead; tusschen 2 loodwanden van 24 cm dikte A 21—27 Mei = between 2 lead-walls of a thickness of 24 cms A May 21—27; B 23—28 Juni = B June 23—28; A 22—28 Juni = A June 22—28.

Fig. 1. Variation of the penetrating rays during the day.
Electrometer unprotected, in lead and between lead-walls.

curves given in fig. 1. It is evident from the two curves, that there is a variation in the radiation with a minimum at ca 8 o'clock in the morning.

A second measurement was made as follows. The electrometer *A* was put on a sheet of lead of a thickness of 10 cms, protected on both sides by two lead-walls of a thickness of 24 cms, a length of 75 cms and a height of 70 cms, arranged in the direction of the meridian.

The electrometer was read during 6 days with intervals from 2 to 4 hours. The results of these observations are likewise given in fig. 1. The upper of these two curves gives the observations from May 21 to May 30. The lower curve gives the observations from June 22 to June 28. These two curves give another distinct minimum and this has not shifted with siderial time. Moreover the intensity (much less now, as only about a fourth part of the radiation could reach the apparatus) has been modified again between May and June and this variation is apparently identical for the whole sky. This result also evidently tends in the same direction.

A similar minimum was also found with apparatus *B*, placed between the lead-walls during the days from June 23 to 28.

An important observation should however be made. Taking the average values of different rays, we find for intensity of the penetrating rays with apparatus *A* and *B* on various days the following values, expressed in I:

	A	*B*	*B* in 2 cms of lead
Beginning of March	1.27	1.35	
2 May	1.47		0.97
4 „	1.43		0.95
7 „	1.57		1.20
9 „	1.63		1.23
10 „	1.61		1.17
31 „	1.86	1.75	

The observations of May 2 up to and including May 10 were made with both apparatus constantly under identical circumstances, whilst the apparatus stood on different sheets of lead at ca 4 meters' distance from each other. Every value given in the table is the average computed for a whole day. There are no striking mutual deviations in these values in the course of the day.

The values of May 31 are found after the lead-pile was reconstructed. Here therefore is a change of circumstances, though at present there is no occasion to suppose, that this has exercised any influence.

The variation between May 2 and May 10 renders it improbable, that the source of the rays must be found in celestial bodies. For, if this radiation should be generated by definite, limited parts of the sky, a distinct difference should arise between the periods, in which the rays reach the electrometer and those in which they are checked by protection. Now it might be assumed, that the rays were diffused in such a way, that the direction has absolutely got lost at the surface of the earth, as for instance in a dense haze the sunlight grows so diffuse that the direction of the sunbeams cannot be perceived any more. This however is in opposition with COMPTON'S hypothesis of the scattering, in which it appears that the secondary rays with rays of a very short wave-length lie within a very narrow cone, the axis of which lies in the direction of the primary rays.

Another possibility is that the rays should be emitted by a great many nebulae or celestial bodies, scattered over the entire sky. In that case it is possible that in the course of the day there is hardly any variation in the intensity. But in that case the observation from May 2 to May 31 indicates, that a change of intensity may arise, which change is about equally great *in all directions*. That this change should occur simultaneously in all radiating celestial bodies, cannot possibly be assumed.

If therefore the observed change is actually due to the penetrating radiation from above, as must be accepted without doubt, *it cannot but be generated in the higher regions of the atmosphere*. This supposition is confirmed by the observations, given in the 3 lower curves of fig. 1. For, indeed, it also appears from these observations, that after a month the distinct minimum is found in the same place, while the entire value over all the twenty-four hours has increased with an equal amount. Here too there is an identical change in all directions. It is clear, that also the position of the milky way had no influence on the intensity of the radiation.

§ 6. *Number of ions, conductivity, earth-charge.* The minimum that appears to occur at Bandoeng at about 8 o'clock in the morning in the intensity of the penetrating radiation, must of course make itself felt in the number of ions, found in the atmosphere. This will also amount to a minimum at that point of time. Together with this the conductivity of the air will be reduced. And finally this will influence the earth charge, which will be temporarily increased by it.

These magnitudes were being recorded at Bandoeng for over a year and the curves indicating the daily variations have been jointly given in fig. 2 in a monthly average. The details of these measurements were previously communicated [1]). The measurements over the whole year will shortly be published. The upper, solid lines in figure 2 denote the conductivity, the value of which has been given to the right of the graph. The two solid lines lower down in the figure, give the number of recorded ions. The value of these per cc has been denoted to the left of the graph.

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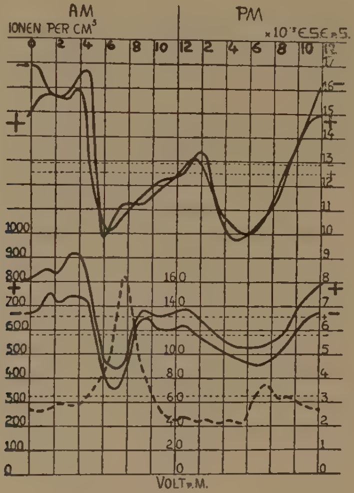
[1]) J. CLAY, Record of electrical conductivity and content of ions of the atmosphere. Proc. Nat. Sc. Congr. Weltevreden 1926, p. 128.

In these curves the strong minimum at about halp past seven is in evident accordance with the minimum found for the penetrating rays. Lastly the dotted curve at the foot of the figure gives the potential gradient in Volts per meter.



Ionen per cm^2 = ions per cc.

Figure 2. Conductivity and number of ions . in the atmosphere. Potential gradient.

The scale of the graph has been drawn in the middle. The maximum is particularly clear in this line.

Finally it may be observed that the course of these curves is fairly identical over the whole year. This is connected with the uniform atmospheric condition during the whole year.

§ 7. *Absorption.* With both apparatus absorption measurements were made. The electrometers were placed on a sheet of lead of a thickness of 10 cms and surrounded at the sides and at the top by a layer of lead of successively 3.5, 7, 10.5, 14, 24, 36 and 48 cms. This lead had been employed in the boilers of stearine-factories for some years, removed, fused into loaves of about 25 Kgrs and next planed off to equal dimensions. The results of these measurements are found in figure 3. The solid line gives the series of measurements with apparatus *A*, in which the average of a day is taken for every value, whilst the dotted line renders the series of measurements made with *B* between May 22 and June 11, where every value represents the average of two or more days.

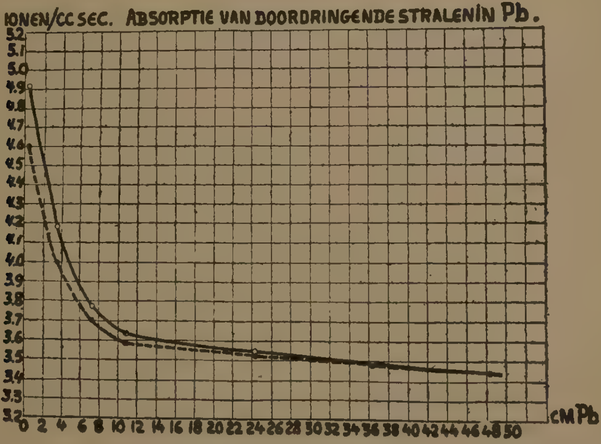
On the whole the mutual deviations of the measurements obtained with apparatus *B* are slighter than those with apparatus *A*. Of the 109 observations made with *B* during these measurements, the deviation of the averages as calculated separately for each absorption-layer, amounts to 0.078 I.

The deviations within thick lead-armourings are as a rule still slighter, which is also connected with the fact that the measurings were continued over longer periods, e.g. from 4 to 6 hours. So the average deviation of the average was but 0.02 I in a lead-armouring of 48 cms.

In order to compare the measurements with the apparatus *A* with those made with *B*, the value found was every where reduced with an amount of 1.19 I, which made the amount of the ionisation in the 48 cm. lead-armouring identical for apparatus *A* and *B*. (In a previous determination (see § 4) 1.25 I was found as the difference in residual radiation between *A* and *B*).

From the course of the curves it is evident, that we have to deal with a mixture of at least two kinds of rays, as was also stated by MILLICAN and CAMERON [1]. For this reason two absorption-coefficients were computed, one for the absorption by layers up to 10 cms of lead, and one for the absorption by layers from 24 to 48 cms of lead. The values found are : $\mu_1 = 0.198$ cm^{-1} and $\mu_2 = 0.045$ cm^{-1}.

The mass-absorption-coefficients, usually given, are: $\frac{\mu_1}{\varrho} = 17.10^{-3}$ cm^{-1} and $\frac{\mu_2}{\varrho} = 4.10^{-3}$ cm^{-1}. These values are greater than those found by MILLICAN and CAMERON. For water they found a mass-absorption-coefficient of $3.0 \,.\, 10^{-3}$ cm^{-1} and of $1.8 \,.\, 10^{-3}$ cm^{-1}. If we assume, that



ionen = ions; Absorptie van doordringende stralen in P_b = Absorption of penetrating rays in P_b

Figure 3. Absorption of the penetrating rays through lead.

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[1] R. A. MILLICAN and G. HARVEY CAMERON, Phys. Rev. Vol. 28, p. 851, 1926.

the scattering (the proper direct absorption is of secondary importance in these short waves) depends on the number of electrons present in the substance per volume-unit, the value must be multiplied with the ratio of the atomic number divided by the atomic weight to enable us to compare with the diffusion in lead; the figures for water therefore should have to be multiplied by 0.72, so that the mass-absorption-coefficient for lead should become in MILLICAN : $2.2 \cdot 10^{-3}$ cm^{-1} and $1.3 \cdot 10^{-3}$ cm^{-1}. These values have been obtained at an altitude of 760 meters.

In his synoptic paper BÜTTNER [1]) gives for his measurements for lead the values lying between $12.4 \cdot 10^{-3}$ cm^{-1} and $3.4 \cdot 10^{-3}$ cm^{-1}.

For the hardest rays HOFFMANN and STEINKE [2]) found still slighter values for the absorption in lead, when they had previously been purified by a layer of lead from the soft part due to scattering.

HOFFMANN found : $\frac{\mu}{\varrho} = 0.41 \cdot 10^{-3}$ cm^{-1} in layers from 20 to 40 cms of lead.

STEINKE gives: $4.5 \cdot 10^{-3} < \frac{\mu}{\varrho} < 7.0 \cdot 10^{-3}$ for layers from 0 to 10 cms of lead.

$0.40 \cdot 10^{-3} < \frac{\mu}{\varrho} < 1.0 \cdot 10^{-3}$ for layers from 20 to 60 cms of lead.

For comparison it may serve, that the gamma-rays of radium C, which have a wave-length of 0.022 Angström, have for lead a mass-absorption, coefficient : $\frac{\mu}{\varrho} = 46 \cdot 10^{-3}$ cm^{-1}, from which it appears, that also the softer component of the penetrating radiation is considerably harder than the gamma-rays of radium C.

For a determination of the wave-length by means of the absorption-coefficient we can use COMPTON'S theory for the scattering of X-rays, if we may assume that the very short wave-lengths with which we have to deal here, the phenomenon is of the same nature as for X-rays. According to COMPTON the scattering will predominate over the so-called absorption with short wave-lengths and the relation between absorption and wave-length may be expressed by the formula :

$$\sigma = \sigma_0 \frac{1}{1+2a}$$

in which σ_0 represents the scattering according to the classic theory of J. J. THOMSON and

$$a = \frac{h}{cm\lambda} = \frac{A}{\lambda} = \frac{0,0242}{\lambda}$$

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[1]) K. BÜTTNER, Z. f. Geophysik **3**, p. 161, 1927.

[2]) E. STEINKE, Z. f. Physik. **42**, p. 601, 1927.

The relation will presumably be better rendered by DIRAC's [1]) formula, which is reduced for the very short wave-lengths to [2]) :

$$\sigma = \sigma_0 \frac{3}{4\,\alpha}.$$

For the short wave-lengths with which we have to deal here, the difference between this formula and COMPTON's is evident, which is essential as soon as the cause of the radiation is sought for.

We can now compute the wave-length from the formula :

$$\frac{\mu}{\varrho} = \sigma_0 \frac{ZN}{A} \cdot \frac{3}{4\alpha}.$$

Here $\sigma_0 = 6.60 \,.\, 10^{-25}$, as has appeared from the measurements concerning the scattering of the X-rays. Z is the atomic number. $N = 6.06 \,.\, 10^{23}$, the AVOGADRO-constant. A is the atomic weight, ϱ the density. For lead is

$$\mu = 1{,}80 \,.\, \frac{3}{4} \frac{\lambda}{0{,}0242} = 60\,\lambda.$$

therefore :

$\lambda_1 = 3\,X$ units ($X = 10^{-11}$ cms), according to COMPTON $\lambda_1 = 6\,X$.
$\lambda_2 = 0.8\,X$ according to COMPTON's formula $\lambda_2 = 1.3\,X$.

§ 8. *Measurements at a greater altitude.* Measurements were made with the apparatus on two different days with the aid of an aeroplane kindly put at our disposal by the Military Air-department of Bandoeng. Apparatus A was unprotected during these measurements, apparatus B was protected by a lead-armouring of a thickness of 2 cms. On April 7 measurements were made, whilst each time the machine was kept at the same level for half an hour. During the second flight on June 15 the machine was constantly kept at a level of 3000 meters for an hour and 20 minutes. This latter was done because on May 13 and 14 measurements had been taken on the summit of the extinct volcano the Pangerango near Buitenzorg, the summit of which is 3024 meters high and because the values bound there did not conform with the observations in the air by aeroplane at the same level. During the second flight however the observation during the first flight was corroborated.

In the table on the next page the values have been given of the intensity of the radiation after being reduced by the ionisation of earth-radiation as found in the vicinity of the laboratory and the residual radiation.

On this subject various remarks can be made. Firstly it is strange that the radiation-intensity at an altitude of 1000 and 2000 meters is less than

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[1]) P. A. M. DIRAC, Proc. Roy. Soc. A. **111**, p. 422, 1926.

[2]) H. A. KRAMERS kindly pointed this out to me.

Altitude in meters	Apparatus *A* unprojected		Apparatus *B* in 2 cms of lead	
	April 7	June 15	April 7	June 15
700	1.67		2.16	
1000	0.95		4.01	
2000	0.80		1.92	
3000	4.73	4.84	3.63	3.77
4000	10.95		6.99	
4300	14.05			

at an altitude of 700 meters on the ground. We get a strong impression that there is a secondary radiation, also radiated upwards by the earth, or that the earth also emits a penetrating radiation. Secondly the values for the apparatus placed in lead are also peculiar at an altitude of 2000 meters, the more so, as the values found during the second flight at 3000 meters, which are especially trustworthy, because the machine continued at the same altitude so long, entirely corroborate the first values. New experiments must necessarily be made to explain this behaviour in the lower regions of the atmosphere. It might be, that we have to deal here with an increase of ionisation owing to a check on the swift electrons, which may be produced by the scattering of the primary rays. V. HESS [1]) had searched for this effect, but all his experiments have had a negative result, just as BÜTTNER'S [2]), nor did I find this increase in other experiments with 0.5 and 1 cm. of armouring. For the rest the values observed at 3000 meters correspond very well with V. HESS'S, the discoverer of the rays, in 1911/1913 [3]), KOLHÖRSTER'S in 1913, MILLICAN'S in 1923 and BÜTTNER'S in 1927. From the difference of the ionisation, found in the two apparatus, we can compute for the absorption in 2 cms of lead an absorption-coefficient : $\mu = 0.13$ at 3000 meters.

The second series of measurements was made at Tjibodas at the foot of the Pangerango at 1400 meters and on the summit at an altitude of 3024 meters. By means of a sheet of lead of 3 cms under the apparatus the earth-radiation was determined in the two places. Assuming the absorption-coefficient to be identical with that of the gamma-rays of *Ra C*, we found 0.83 I for the earth-radiation at an altitude of 1400 meters and 0.88 I on the summit. This is uncommonly little, but easily explained by the young-volcanic character of the mountain.

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[1]) V. F. HESS, Sitzungsberichte der Ak. d. Wiss. Wien, p. 634, 1927.

[2]) K. BÜTTNER, Zeitschrift f. Geophysik **3**, p. 883, 1927.

[3]) Verg. V. F. HESS, Die elektrische Leitfähigkeit der Atmosphäre und ihre Ursachen 1926, p. 115 and following.

At Tjibodas 4 observations were made with apparatus *A* before climbing the mountain, which yielded an average of 1.51 I with an average deviation of 0.03 I and after the descent 7 observations were made, yielding an average of 1.50 I with an average deviation of 0.16 I. On the summit 13 observations were made during 36 hours, yielding an average of 3.28 I with a deviation of 0.32 I, i.e. the variations found here were greater than those regularly occurring at Bandoeng, but amounted to 20 % at most.

With apparatus *B* 4 measurements were made at 1400 meters, yielding a value of 1.30 I with an average deviation of 0.13 I, whilst on the Pangerango with apparatus *B* 3.15 I was found due to the penetrating radiation with an average deviation of 0.10 I.

In an armouring of 3 cms of lead 1.03 I was found with the same apparatus at 1400 meters and 2.88 I at 3024 meters. From these values combined with the data for apparatus *A* an absorption-coefficient was computed of $\mu = 0.10$ at 1400 meters and $\mu = 0.095$ at 3024 meters.

At the same altitude in the flying-machine there were observed 1.56 I more than on the mountain-top. Of course it is possible, that the intensity is changed during those various days, though it is to be doubted that the amount would be so high. With subsequent measurements it will be necessary, that regular control-measurements are made at a definite station. Finally it should be observed, that the minimum ever present on the Bandoeng plateau was *not* perceived here. On another side of the mountain at 1230 meters from an average of 5 observations 1.23 I was found for the penetrating radiation. That the value in this case and as mentioned above, at Tjibodas at 1400 meters was found to be so slight, will doubtlessly be attributable to the protection of the mountain, which intercepts the radiation of a considerable part of the sky.

§ 9. *Observations in other places.* In order to determine to how much the residual rays of the apparatus *B* precisely amounted; I took it to Europe for the purpose of making a determination in a rock-salt-mine, which might be expected to be quite free from radiation.

On the way a series of measurements was made on the boat-deck of the steamer *Slamat*, about 14 meters above the sea-level, from the Red Sea to and partly including the Mediterranean. It is a remarkable fact, that an increasing value of the radiation was stated, which may be partially the result of increased gammaradiation of the emanation in the atmosphere.

It might have been that the residual radiation in the apparatus increased. As will presently appear this is however unlikely.

On Oct. 31 and Nov. 11 I had the privilege of collaborating with W. KOLHÖRSTER in the Berlepsch Schacht of the Stassfürter-salt-mine. On the ground over the mine an ionisation was found of successively 7.95 I, 7.98 I, and 7.99 I and after the measurements in the mine of 8.14 I. In the mine

400 M. below the earths surface surrounded by a layer of rock-salt of 80 to 100 meters we found 4.90 I and 4.93 I in the large „Festsahl" and in a part, where there was some salt of potassium in the vicinity, we found 5.13 I. Seeing formerly at Bandoeng in a lead-armouring of 48 cms 3.44 I was found, there were two possibilities, either the residual radiation of the electrometer had increased (the apparatus had never been open during any measurement), or that the rock-salt was not free from radiation. Lucky circumstances however enabled me to exclude the first possibility as highly improbably.

Date	Time	Place	Ionisation + residual radiation
23 July '27	14 h. 3 m.—17 h. 7 m.	Red Sea	5.17
	17 h. 7 m.—19 h. 27 m.	„	4.83
	19 h. 27 m.—24 h.	„	5.22
24 July	0 h. — 5 h. 26 m.	„	5.82
	5 h. 16 m.— 8 h. 40 m.	„	5.98
	8 h. 52 m.—14 h. 28 m.	Bay of Suez	6.68
	14 h. 29 m.—17 h. 42 m.	„	6.18
	17 h. 43 m.—19 h. 42 m.	Canal of Suez	6.21
	19 h. 42 m.—24 h.	„	6.50
25 July	0 h. — 3 h. 55 m.	„	6.77
	11 h. 58 m.—14 h. 54 m.	Mediterranean	6.56
	17 h. 12 m.—18 h. 49 m.	„	6.56
26 July	8 h. 38 m.—12 h. 9 m.	„	7.20
	12 h. 11 m.—16 h. 31 m.	„	7.16
	16 h. 31 m.—19 h. 7 m.	„	7.38
27 July	8 h. 33 m.—10 h. 52 m.	„	7.00
	10 h. 52 m.—14 h. 16 m.	„	7.62
	14 h. 16 m.—17 h. 5 m.	„	7.14
	17 h. 15 m.—20 h. 37 m.	„	7.42
28 July	8 h. 26 m.—11 h. 13 m.	„	7.75
	11 h. 13 m.—13 h. 10 m.	„	7.72
	13 h. 10 m.—14 h. 50 m.	„	8.03

In Prof. V. HESS's laboratory at Graz Prof. HESS kindly gave me the opportunity of making a measurement in an iron-armouring of a thickness of 8 cms, through which according to Prof. HESS' experience the gamma-rays of radium do not penetrate.

In this armour on Nov. 10 I found the values 5.37 I, 5.4 I, 5.25 I and 5.20 I, averagely 5.31 I. Seeing that according to Prof. HESS the value of the penetrating radiation at that place should be about 1.9 I, the residual radiation of the apparatus *B* would have a value of about 3.4 I, which is in perfect accordance with the values found at Bandoeng. From this it would follow, that the value of the radiation has gradually increased with the geographical latitude, a result that may correspond with former expectations of various investigators, who searched for the origin of the radiation in the higher regions of the atmosphere [1].

But besides this proves that the rock-salt in Stassfürt is not free from radiation, but that there still exists an ionisation of 1.5 I. KOLHÖRSTER's measurements may also be expected to give a decisive answer to that question.

Bosscha Lab. Bandoeng, 1927.

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[1] V. F. HESS, Die elektrische Leitfähigkeit der Atmosphäre und ihre Ursachen. 1926, p. 123 and following.

b

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